of PCBs, a health questionnaire, liver function tests and other biochemical studies.

Recommend a similar study be carried out in an industrial population exposed to PCBs.

Systematic studies to identify sub-groups of the total U.S. population who consume high levels of fish with more accurate measures of PCB exposure.

Polybrominated biphenyls

Recommend that a large scale epidemiological study be carried out to (1) identify all farm family members from quarantined farms in Michigan, (2) identify those individuals with secondary exposure to PBB contamination through the purchase of dairy products from quarantined farms on a regular basis, and (3) a suitable control group of non-exposed farm families. These groups should be followed to assess any short and long term adverse health effects related to PBB exposure.

Subgroups of these farm families from quarantined farms should be studied by:

1. Repeat PBB blood levels.
2. Matched blood-body fat PBB levels.
3. Pregnant female-infant studies.
4. A battery of biochemical studies.

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Ancillary Studies

Toxicology studies in non-human primates and rodents with hexabrominated biphenyl and any brominated contaminants of hexabrominated biphenyls.

Toxicology studies in several animal species (mice, rats, dogs, non-human primates using hexabrominated biphenyl and several PCBs to determine species differences in response to the effects of these compounds.

Toxicology studies feeding hexabrominated biphenyls and selected PCBs singly and in combination to determine if there are different or additive effects when fed in combination.

CHEMISTRY OF PCBs AND PBBs

I. Introduction

A recent book by Hutzinger et al. (1974) reviews the chemistry of chlorinated biphenyls through the end of 1973. This wide-ranging review also includes discussions of metabolism and determination of chlorinated biphenyls.

The present report reviews areas of chlorobiphenyl and bromobiphenyl chemistry held to be pertinent to the Subcommittee's concern for possible health effects of these types of compounds. No attempt at complete coverage of these subject areas is claimed. Findings reported since 1973 are particularly stressed.

Non-metabolic alteration of the halogenated biphenyls is considered in terms of agents most available to induce chemical change in the environment. Expected differences between chlorinated biphenyls and brominated biphenyls in their environmental chemistry are commented on.

It is possible that certain of the chlorinated biphenyl compounds will be shown to have relatively greater potential hazard for health. Therefore, occurrence and fate in the environment and metabolism and toxic effects in animals are related to chemical structure of the biphenyls.

For the general public, food is presumed to be the major

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source of chlorinated biphenyl compounds. The important concepts related to analytical methodology for PCB (and PBB) residues, particularly in foods, are reviewed. Alternative means of quantitation of these residues and problems in the quantitation techniques are discussed.

The pertinent aspects of chlorinated dibenzofurans, as known contaminants in commercial PCBs and as potentially significant environmental contaminants, are reviewed.

In reviewing the chemistry related to health effects of the PCBs and PBBs, it must be remembered that environmental contamination by these two commercial chemical mixtures is vastly different in magnitude. The former have been steadily released into the environment, in many countries, presumably over decades, and are now found to be a pervasive, world-wide contaminant. The number of chlorinated biphenyls reaching the environment probably number nearly 100 different compounds. The PBBs, encompassing a small number of chemical structures to begin with, are of concern due to a single, fairly recent contamination incident, apparently limited to the State of Michigan.

II. Chemistry of Chlorinated Biphenyls

A. Synthesis and Analysis of Commercial Mixtures

Commercial preparation of mixtures of chlorinated biphenyls by reaction of biphenyl with chlorine has been described by Hubbard (1964). A more recent discussion of this subject,

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including the newer preparation designated as Aroclor 1016, is now available (Mieure et al., 1976). Analysis of the chlorinated biphenyl content of various American commercial PCB mixtures (Aroclor) has been reviewed by Hutzinger et al. (1974). An estimated 40 to 60 different chlorinated biphenyl compounds are present in each of the higher chlorinated commercial mixture. (There are 209 possible compounds obtainable by substituting chlorine for hydrogen on from one to ten different positions on the biphenyl ring system; see Appendix.) PCB commercial mixtures produced in the U.S. and elsewhere have been shown to contain classes of compounds other than the chlorinated biphenyls: chlorinated napthalenes and chlorinated dibenzofurans (Cl-DBFs), for example (Vos et al., 1970; Roach and Pomerantz, 1974 a,b; Bowes et al., 1975a). The possibility that naphthalene and dibenzofuran contaminate the technical biphenyl feedstock used in preparation of the commercial PCB mixtures has not been excluded.

Available toxicity information indicates that, of the identified types of contaminants in commercial PCB mixtures, Cl-DBFs pose the greatest potential hazard (See Section II.E on Chlorinated Dibenzofurans). As a result, the Cl-DBFs have become the focus of studies on contaminants in these mixtures. No report has appeared of an attempted complete content analysis of the trace impurities in a commercial PCB mixture.

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B. Non-metabolic Alteration of Chlorinated Biphenyls

Chlorinated biphenyls, as is typical of aryl chlorides generally, are quite stable to chemical alteration. Consideration of possible non-metabolic alteration routes for these compounds in the environment suggests air oxidation, aqueous hydrolysis, and photoalteration in sunlight as potential reactions to be investigated. (Thermal decomposition would be of concern in connection with incineration conditions meant to destroy waste chlorinated biphenyls). Study of these reactions under the complex and variable sets of conditions existing in the environment is difficult. Chemical reactivity of chlorinated biphenyls has therefore been studied almost entirely under the more controlled conditions of the laboratory.

Oxidation

PCBs are fairly stable to oxidation under moderate conditions. PCBs are stable under conditions which easily oxidize DDE, and can be separated from DDE by oxidizing DDE to the more polar dichlorobenzophenone prior to column chromatographic separation (Trotter, 1975). To effect the oxidation of DDE, the PCB-DDE solution is refluxed in 2.5% chromic acid-acetic acid on a steam bath. Some of the lower chlorinated biphenyls, however, are not recovered after the oxidation. It is reported (Weingarten, 1961) that mono-, di-, and trichlorobiphenyls are oxidized in 7.5%

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chromic acid-acetic acid to their respective (chloro-) benzoic acids. With vigorous oxidizing conditions in the environment, some PCB oxidation, especially of the lower chlorinated biphenyls may occur. It is difficult, however, to assess the total extent of possible environmental oxidation of PCBs.

Hydrolysis and Alcoholysis

PCBs are fairly stable to hydrolysis under moderate conditions. When refluxed with 2% KOH in ethanol, PCBs are stable (Trotter, 1975; Young and Burke, 1972). A halogen on a chlorobiphenyl molecule is not easily displaced in a nucleophilic substitution reaction. Under vigorous conditions the 4 and the 4,4' positions of decachlorobiphenyl are found to be the most susceptible to chlorine displacement by hydroxide and methoxide ions. Decachlorobiphenyl can be hydrolyzed to octachloro-4,4'-biphenylol when treated with aqueous alkali at high temperatures in an autoclave (Smith, 1948; Societe d'Electro Chimie, 1962). Heating 2,5-dichlorobiphenyl with sodium methoxide produces 2-chloro-5-biphenylol (deCrauw, 1931). Decachlorobiphenyl when treated with sodium methoxide in pyridine yields the 4-methoxy- and 4,4'-dimethoxy-chlorobiphenyl (Binns and Suschitzky, 1971). It is probable that the non-metabolic hydrolysis or alcoholysis of PCBs in the environmen is limited.

Photochemistry

Exact environmental conditions for the photochemistry of

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environmental contaminants, including PCBs, are sometimes difficult to simulate in the laboratory. Limited understanding exists concerning the parallel of laboratory photoreactions and reaction rates under non-environmental conditions and possible environmental photolyses. The exact environmental conditions under which residues may photoreact can be diverse and difficult to evaluate. Unknown or discounted factors in the environment, such as possible sensiters or quenchers, may be important. The frequency (energy) and intensity of a laboratory photolysis light may not be comparable with environmental conditions. 3000 Å probably represents the practical lower limit of the ultraviolet (UV) portion of sunlight (Crosby, 1969). The residue must be exposed to sufficient light to react appreciably. It is necessary to consider the physical state of the residue exposed to light in the environment. The residue may exist as a solid or liquid (e.g., a film), a solution or a vapor. In photolyzing solutions the solvent can have an important effect. Photoreactions which proceed in one solvent may not proceed or may proceed at a different rate in another solvent. A muddy river containing a residue may yield different results compared to a laboratory photolysis in hexane. Laboratory photolyses under a variety of conditions which simulate most, if not all, of the environmental conditions of photolysis could be extremely significant and relevant. In the absence of these, we must rely on the questionable extrapolation of laboratory photolyses under non-environmental conditions.

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The photochemistry of PCBs has been described by Hutzinger, et al.,(1972; 1974). In contrast to oxidation and hydrolysis, PCBs are fairly easily photoreacted under certain laboratory conditions. PCB photochemistry has been studied in various solutions, as a thin film, and as a vapor. In hydrocarbon solvents progressive reductive dechlorination of the PCB is the predominant photochemical reaction (Hutzinger et al., 1974). Irradiation of solutions of chlorobiphenyls (Hutzinger et al., 1972) and trapped gas liquid chromatographic (GLC) effluents (Hannan, et al.,1973) have shown that PCBs with higher chlorine content dechlorinate more readily. 0.1% hexane solutions of 2,2',5,5'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl were each irradiated with 3100 Å light in a Rayonet reactor (Hutzinger et al., 1972). After 24 hours of irradiation, 33% of the 2,2',5,5'-tetrachlorobiphenyl was unreacted while < 1% of the 2,2'4,4',5,5'-hexachlorobiphenyl remained. In dechlorinating PCBs by photoexcitation, ortho chlorines preferentially cleave (Ruzo et al., 1974). With PCBs containing only meta and para chlorines, meta chlorines are lost preferentially. The rate of dechlorination is faster in alcohol solvents, such as methanol (Hustert and Korte, 1972) than in hydrocarbon solvents. Irradiation of 2,2',4,4',5,5'-hexachlorobiphenyl in methanol yields, in addition to reductive dechlorination, ring methoxylation (Ruzo et al., 1974). Photochemical studies of PCBs in aqueous solutions may offer a significant relevance to environmental PCB photochemistry. A 0.4% Aroclor 1254 suspension in water-dioxane (7+3) in the presence of sodium bicarbonate with

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air bubbling through the mixture was irradiated with 3100 Å light. Two thin layer chromatographic fractions of the Aroclor 1254 after irradiation corresponding to the "addition of water to chlorobiphenyls" and a "carboxy fraction" were found (Hutzinger et al., 1972). Presumably PCBs formed by reductive dechlorination were also produced. Black light irradiation of Aroclor 1254 as a thin layer film in the presence of water yields a "carboxy fraction" and a fraction whose mass spectrum indicates hydroxychlorobiphenyls (Hutzinger et al., 1972). Sunlight irradiation of certain chlorobiphenyls as a thin film without the presence of water gives reductive dechlorinated products (Hutzinger et al., 1974). Chlorinated terphenyls and quaterphenyls are also produced by the black light and sunlight irradiation of certain chlorobiphenyls as a thin film (Hutzinger et al., 1974). Vapor phase photolysis of PCBs may be extremely relevant especially for the more volatile components of Aroclors with low chlorine content. Sunlamp irradiation of the vapor phase of a refluxing suspension of 2 2',5,5'-tetrachlorobiphenyl and water yields "carboxy" products (Hutzinger et al., 1972).

These laboratory photoreactions represent chemical conversions which may proceed in the environment. The photoreaction rates under diverse environmental conditions and the extent of PCB degradation or reaction in the environment are extremely difficult to assess.

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The reported low-yield conversion of certain chlorinated biphenyls to Cl-DBF is discussed under Chlorinated Dibenzofuran, Section II.E.

C. Chemical Structure Related to Occurrence, Fate and Effects of Chlorinated Biphenyls

The physical and chemical properties of chlorinated biphenyl compounds and commercial mixtures of PCBs vary greatly depending on the degree and position of chlorine substitution on the biphenyl ring system. Of particular importance to their environmental occurrence and fate are the properties of volatility, water solubility, bioaccumulation, biodegradability and photostability. Volatility, water solubility and bioaccumulation are of more importance as mechanisms of introduction into and transport within the environment. Biodegradation and photodegradation are more important as mechanisms of removal.

There is data (Mieure et al., 1975) which indicates that the higher chlorinated biphenyls are less volatile and less water soluble than the lower chlorinated biphenyls. These two factors would tend to enhance the ratio of lower to higher chlorinated biphenyls in the environment. There is no clear data to assess the involvement of chlorine position in volatility and water solubility, but is likely to be of less importance. Therefore, the lower chlorinated biphenyls are more likely to volatilize into and be selectively transported in the aqueous environment.

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The relationships between structure and bioaccumulation factors for PCB isomers are only beginning to be assessed (McKinney, 1975; Sugiura et al, 1975) with the availability of purified specific isomers for study. However, it appears (Zitko et al., 1972; Veith, 1975) that the peak patterns from gas chromatography found in environmental samples representing the biosphere most closely resemble the higher chlorinated commercial mixture, Aroclor 1254. This suggests a selective accumulation of the mores highly chlorinated components of the commercial mixtures in biological material. This also indicates that the higher chlorinated biphenyls are able to find their way into the environment in spite of their poorer volatility and water solubility. Pharmacokinetic studies (Matthews, 1975) with selected radiolabeled chlorinated biphenyl compounds have confirmed the trend toward increasing biological half-life with increasing chlorine number. However, these findings may be the result of both higher accumulation rates and lower elimination rates for the higher chlorinated biphenyls. It may be of interest to note that fish from lower and intermediate levels of the food web have been found (Zitko et al., 1972) to contain lower amounts of hexa and higher amounts of tetra and penta than higher trophic level white and silky sharks and aquatic birds This suggests that selectivity in bioaccumulation is also a function of biospecies.

Again the effects of varying chlorine position are less

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clearly understood, and the best assessment of this comes from study of two or more members of an isomeric series of the chlorinated biphenyls. Recent work with five symmetrical hexachlorobiphenyl isomers in chicks (McKinney et al., in press; Goldstein et al., in press) and subsequently in mice (Biocca, 1975) has demonstrated that separate and distinct differences in isomer toxicity are possible and that the differences are related to chemical structure via effects of varying chlorine substitution on compound lipophilicity and metabolism. The hexachloro isomers studied were 3,4,5,3',4',5'-; 2,4,6,2',4',6'-; 2,3,4,2',3',4'-; 2,4,5,2',4',5'-; 2,3,6,2',3',6'- and 2,3,5 2', 3',5'-. Those hexa-isomers with 4,4'-substitution appear to be more rapidly accumulated and may be more slowly metabolized, i.e., these isomers showed greater accumulation in adipose tissue and increased activity in the liver and overall greater toxicity. These differences are believed to be associated with differences in molecular polarizability and to be measureable by spectroscopic and chromatographic techniques.

Other workers (Ax et al., 1976; Ax and Hansen, 1975) have compared the toxicity of two pentachlorobiphenyls in laying chicks. The isomer with 4,4'-substitution (2,4,5,3',4') showed higher average embryonic mortality and teratogenicity in unhatched eggs but lower decreased fertility in the chick than 2,3,6,2',3' the isomer not chlorinated in the 4-position. Although it is difficult to assess the role of metabolism here, the data would suggest a

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more rapid accumulation of the 2,4,5,3'4'-isomer in the egg. Other workers (Bush et al., 1974) have already observed a correlation between PCB content of eggs and embryo mortality and teratogenicity.

Various other workers (Ecobichon and Comeau, 1975; Johnstone et al., 1974; Hill et al., 1974) studying a range of chlorinated biphenyls have generally observed the importance of degree of chlorination as well as position of chlorine substitution (especially 4,4'-substitution) in overall biological effectiveness. Although some of the compounds studied are unrealistic as components of commercial PCB mixtures, they have served as models to demonstrate the importance of chlorine number and position. Nevertheless, of 50 possible components of Aroclor 1254 identifed by Sissons and Welti (1971) as many as 19 (38%) could have 4,4'-substitution. It is of interest to note here that one of the possible persistent isomers found in *Yusho* patient tissue has been tentatively identified (Kuratsune, 1975) as the 2,3,4,5,3',4'-heptachlorobiphenyl. This isomer has been prepared (McKinney, personal communication) and its toxicty will be determined especially in relation to the highly toxic 3,4,5,3',4',5'-hexa isomer previously tested.

It has been only recently that hydroxylated metabolites of PCBs have been isolated and identified (Jansson et al., 1975) in environmental samples. The study of the metabolism of the commercial mixtures (deFreitas and Norstrom, 1974) themselves has

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received little attention for obvious reasons. Recently, the metabolism of purified chlorinated biphneyls, some radiolabeled for quantitation purposes, has been studied in a number of biological systems. Although there are a large number of publications in the literature on this subject, this report will concern itself with those studies which seem to support generalities in terms of the effects of varying chlorine number and position on metabolism with particular reference to mammalian systems and to realistic components of Aroclors.

The distribution and excretion of a series of four radiolabeled (^{14}C)chlorobiphenyls which have degrees of chlorination similar to and are themselves constituents of Aroclors 1221, 1242, 1254, and 1260 have been studied (Matthews, 1975) in the male rat. These studies have clearly shown an increasing biological half-life with increasing chlorine number for the series (4-; 4,4'-; 2,4,5,2',5'- and 2,4,5,2',4',5'-) which is believed to be related to the rate of metabolism and the ease of formation of the arene oxide intermediate. These compounds were also dosed at realistic exposure levels (0.06 to 6.0 mg/kg) which showed that little if any of the chlorobiphenyl is excreted in unchanged form. Most other metabolic studies (Hutzinger et al., 1974) with selected chlorobiphenyls have dealt with much higher dose levels (generally resulting in excretion of much unchanged biphenyl) and unlabeled compounds which are of little quantitative value in assessing the effects of chlorine degree and position.

There has been no similar study with selected chlorinated biphenyls within an isomeric series to assess the effects of chlorine position on metabolism with the possible exception of an incomplete study (Hass et al., unpublished) on the identification of metabolites from the excreta of chicks (and mice) fed symmetrical hexachlorobiphenyl isomers. It is essential that this be done with symmetrical isomers (in order to simplify the probelm of interpretation) and preferably in two or more isomeric series (tetras and hexas).

The various metabolism studies have generally shown the occurrence of polar hydroxylated compounds as major components of the metabolite mixture. As the degree of chlorination increases, hydroxylation can be concurrent or concomitant with dechlorination (Hutzinger et al., 1974). There is also evidence for the formation of methyl ethers (Safe, 1975) and methylchlorobiphenyls (Hass et al., unpublished) as metabolites.

There is an increasing body of evidence (Safe et al., 1975) to support the arene oxide intermediate in hydroxylation, especially (Chen et al., Division of Nutrition and Disposition, in press) in cases where vicinal (1-2,-adjacent) unsubstituted carbons are found in the molecule. The corresponding dihydrodiol and/or catechol generally occur along with the phenolic metabolites.

Althought it has not been studied in mammalian systems, there is at least one report (Baxter et al., 1975) that studies of

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individual chlorinated biphenyls do not accurately predict the rates of metabolism of the same compound in simple mixtures. Therefore, the overall problem of metabolic degradation of the commercial mixtures may be complicated by the possibility that certain PCBs are potent enzyme inducers but poor substrates and vice versa with various degrees in between. This is further complicated by the fact that certain chlorinated biphenyls occur in optically active forms and only one enantiomer may be biologically active and undergo enzyme interactions. The existence of nine of the major, and ten of the minor, constituents of Aroclors 1242, 1254, and 1260 in optically active forms has been predicted (Kaiser, 1974).

D. Determination of PCB Residues

The determination of PCB residues has been reviewed in detail by the WHO Task Group report on "Environmental Health Criteria for Polychlorinated Biphenyls and Terphenyls" (WHO Task Group, 1975) and in "Chemistry of PCBs" (Hutzinger et al., 1974).

PCBs are lipophilic, quite similar in this respect to DDE, the metabolite of DDT. An analyses for PCB residues follow procedures the same as or similar to those used for multiple residues of organochlorine pesticides (WHO Task Group, 1975; Hutzinger et al., 1974; Food and Drug Administration, 1968-1975, Horwitz, 1975; Hearing Clerk, Dept. HEW, 1973). The individual steps that follow sampling are extraction of residues from the sample, isolation of residues from coextractives (cleanup),

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separation of PCBs from interfering chlorinated hydrocarbon pesticides, quantitation, and confirmation of identity. In general analytical methods capable of completely extracting residues of organochlorine pesticides from sample substrates and of quantitatively recovering the pesticides through subsequent cleanup procedures are also capable of achieving quantitative analysis for PCBs. The lipophilicity of chlorobiphenyls which increases with increasing chlorine content may influence their recovery through some analytical methods (Stalling et al., 1972). For example, recoveries through the frequently used cleanup step, partitioning of PCB from a petroleum ether or hexane solution of fat or oil to acetonitrile, exceed 95 percent for Aroclor 1242 but drop to 75-80 percent for Aroclor 1260 (Hearing Clerk, Dept. HEW, 1973). Overall ability of typical analytical methodology to recover PCBs added in vivo to food samples is shown by two interlaboratory studies conducted within the Food and Drug Administration (FDA) and one study conducted for the Association of Official Analytical Chemists (AOAC) (Food and Drug Administration, 1971; Burke, 1972; Food and Drug Administration, 1973; Sawyer, 1973). Using methodology described in the FDA Pesticide Analytical Manual and in the Book of Official Methods of the AOAC, average recoveries and coefficients of variation for determination of Aroclors added as unknowns to different foods were: Aroclor 1254-fish, 74 $\pm$ 9 percent; Aroclor 1254-infant chicken, 89 $\pm$ 22 percent; Aroclor 1242-chicken fat, 101 $\pm$ 13 percent; Aroclor 1248-chicken fat, 96 $\pm$ 9

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percent;Aroclor 1254-fish, 75 ± 14 percent; Aroclor 1260-fish, 75 ± 15 percent. The three studies involving fish required separation of the PCBs from the DDT group before quantitation.

Gas chromatography with electron capture detection is the most widely used procedure for determination of PCB residues. Gas chromatographic columns with methyl silicone liquid phases are widely used under conditions that typically separate the Aroclors and PCB residues into about 15 peaks (Fishbein, 1972). The 10 percent DC-200 (or OV-101) column described in the FDA Pesticide Analytical Manual separates Aroclor 1254 into 14 peaks (Armour, 1972). These analytical columns do not give a highly defined representation of the Aroclor or PCB residue; several of the peaks in Aroclors result from mixtures of more than one chlorobiphenyl (Sissons and Welti, 1971; Stalling and Huckens, 1971; Webb and McCall, 1972; Webb and McCall, 1973). A column prepared from purified Apiezon L has been shown to separate a 54 percent chlorine PCB mixture into over 40 peaks (Jensen and Sundström, 1974). Separation of the PCB residue into three fractions by chromatography on charcoal prior to examination on the Apiezon L column has made it possible to characterize and quantitate nearly 60 technical PCB components. This method provides a way to get much needed, more detailed information on the compositon of PCB residues and might be used in special studies. The increased time and complexity of this approach would probably limit its application in regular monitoring analysis.

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The need to confirm residue identity and the procedures available are similar for PCBs and pesticides. The multipeak gas chromatographic pattern of a PCB residue may be very similar to that of a commercial Aroclor or, as in most biological samples, the residue peak pattern may be changed to varying degrees from that of a given Aroclor. The use of column chromatographic or chemical reaction procedures to separate PCBs from organochlorine pesticides increases the certainty of the gas chromatographic identification. Procedures readily available to the residue laboratory for confirming the identity of PCBs include: halogen specific gas chromatographic detectors (Hearing Clerk, Dept. HEW, 1973), stability of the residue peak pattern after refluxing the extract with alcoholic alkaline solution (Young and Burke, 1972), perchlorination of the residue to the decachlorobiphenyl derivative (Berg et al., 1971; Armour, 1973), and thin layer chromatography (Fehringer and Westfall, 1971; deVos and Peet, 1971). Mass spectrometry is not readily available to many laboratories conducting analyses for PCBs nor would the expense justify regular use in monitoring programs. However, the use of mass spectrometry is encouraged for residues and samples which are unusual or significant and for the occasional examination of a so-called routine sample.

Two especially critical considerations are associated with the determination of PCB residues: (1) their separation from potentially interfering organochlorine pesticides, particularly

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DDT, TDE, and DDE or the multicomponent chlordane or toxaphene, and (2) quantitative measurement of the multicomponent PCB residue which, in biological organisms, is usually changed in relative amounts of chlorobiphenyl components from commercial Aroclors or which may result from mixture of PCB from different sources. To achieve reliable residue results it is essential that the analyst correctly make critical judgements and interpretations in dealing with mixed residues of PCBs and organochlorine pesticides and in quantitation of the multicomponent PCB residue. There is no substitute for analyst experience in this analysis.

PCBs are separated from certain pesticides in the usual cleanup procedures, e.g., adsorption chromatography on Florisil or alumina or by gel permeation chromatography (Food and Drug Administration, 1968-1975; Stalling et al., 1972; Holden and Marsden, 1969). When DDT, TDE, DDE, chlordane, or toxaphene are present, ancillary procedures designed to separate these chemicals from PCBs must be used. The DDT analogs, particularly DDE, are the pesticide residues most frequently encountered in samples and DDE is the most difficult to separate from the PCBs. The effective electron capture gas chromatographic response for DDE is 20-30 times greater than for an equal weight of Aroclor 1254 and the response for DDT is only slightly less than that for DDE (Food and Drug Administration, 1968-1975). Without proper treatment these pesticides can readily interfere in the determination of PCBs. Some procedures utilizing column chromatography

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on alumina or Florisil separate DDT and TDE and intentionally collect DDE and PCBs in the same fraction (Holden and Marsden, 1969; Reynolds, 1969), which is analyzed. In these cases the analyst must exclude the DDE region of the gas chromatogram from the quantitative measurement of PCBs. Column chromatography on charcoal also has been proposed for separation of PCBs from DDE, DDT, and other organochlorine pesticides (Berg et al., 1971). Column chromatography on silicic acid is probably the most widely used procedure for separating PCBs from DDT and analogs (Food and Drug Administration, 1968-1975; Armour and Burke, 1970). The technique is fairly lengthy and difficult to reproduce, requiring empirical standardization in each laboratory (Sawyer, 1973; Masumoto, 1972; Edwards, 1974). The separation of DDE is probably not 100 percent effective but under ideal conditions practically all DDE can be separated; the usual inconsistency is for a portion of the DDE to be eluted from the column with the PCBs, requiring allowances to be made in PCB quantitation. The lower chlorinated PCBs present the greatest difficulty in separation from the DDT group by column chromatographic procedures. DDE can also be separated from PCBs by oxidation to the dichlorobenzophenone, followed by a chromatographic separation of this more polar derivative from PCBs. DDT and TDE may be dehydrochlorinated to their respective olefins and similarly separated along with DDE (Mulhern et al., 1971; Collins et al., 1972; Trotter, 1974). This technique has not received as much application as the chromatographic procedures, probably because pesticides and lower

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chlorinated biphenyls are destroyed or changed, preventing their determination. A variation on this approach used sodium dichromate plus a minute amount of sulfuric acid, rather than dehydrochlorination followed by oxidation with chromium trioxide in acetic acid. The dichromate reagent is reported to convert DDE quantitatively to the dichlorobensophenone without affecting DDT, TDE, or any of the chlorobiphenyls (Jensen and Sundström, 1974).

Quantitation of PCB residues is done in most laboratories by comparison of measurements made on the multicomponent electron capture gas chromatograms of the residue and a known quantity of reference material. The PCB residue in biological samples, as mentioned earlier, is very likely to be changed in the relative amounts of chlorobiphenyl components from any one Aroclor or the residue may be a mixture of PCBs from different sources (Food and Drug Administration, 1968-1975; Jensen and Sundström, 1974; Cook, 1972). The response of the electron capture detector varies with the number and location of chlorine atoms in the biphenyl molecule (Gregory, 1968; Zitko et al., 1971). With the electron capture system described in the FDA Pesticide Analytical Manual, the response/unit/weight increases about 6 fold from Aroclor 1242 to Aroclor 1260 (Hearing Clerk, Dept. HEW, 1973). The halogen specific microcoulometric and electrolytic conductivity detectors respond proportionally to the weight of chlorine present and in theory could provide a more accurate measurement of a PCB residue that is not exactly the

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same composition as the reference (Hearing Clerk, Dept. HEW, 1973). However, lower sensitivity, difficulty in maintaining optimum performance, and limited availability in residue laboratories has limited the use of these detectors. Unless the PCB residue and reference Aroclors are exactly the same in chlorobiphenyl composition, the gas chromatographic determination cannot be considered accurate; the greater the difference between residue and reference composition, the greater the deviation between determined and the true residue level (Hearing Clerk, Dept. HEW, 1973; Beezhoold and Stout, 1973). The most frequently used approaches to quantitation have been selected for the reference the Aroclor with the most similar gas chromatographic pattern to the residue and: (1) compared the response of a single peak in the residue with the response of the counterpart peak in the Aroclor reference; or (2) compared the total response for several peaks from the residue to the total response for the counterpart peaks in the reference; or (3) compared the total response for all peaks in the residue with the total response for all peaks in the reference; or (4) in a greater effort to duplicate the residue peak pattern, prepared a reference made up of one or more Aroclors to simulate the gas chromatographic pattern of the residue, and compared the total response for all peaks of the residue to the total response for all peaks in the reference (Sawyer, 1973; Beezhold and Stout, 1973). Response has been measured in terms of both peak height and area (Sawyer, 1973). The latter approach which utilizes an Aroclor or a mixture

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of Aroclors to duplicate the residue peak pattern is recommended by the AOAC for quantitation of PCB residues in certain foods (Horwitz, 1975). This is a currently accepted and practical way to quantitate PCB residues. Perchlorination of PCBs to decachlorobiphenyl has been suggested as a means to improve precision and consistency in PCB determination (Berg et al., 1971; Armour, 1973). This approach will not improve the accuracy of quantitation, however, because proportions of individual chlorobiphenyls in the PCB residue remain unknown; equal weights of individual chlorobiphenyls of different chlorine content result in different weights of decachlorobiphenyl. Contaminations found in antimony pentachloride, the perchlorination reagent, also detract from this procedure for quantitation purposes (Trotter and Young, 1975). An approach to quantitation which appears to have practical merit as well as offering improved accuracy in quantitation has been advanced by Webb and McCall (1973). The PCB residue is quantitated peak by peak in comparison to reference Aroclors which have been characterized as to the number of chlorines and the fraction of total Aroclor weight represented by each electron capture peak after separation on a widely used (methyl silicone liquid phase) gas chromatographic column. The availability of carefully characterized Aroclors and evaluation in practice are required to fully evaluate the merits of this procedure.

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Precision in the interlaboratory determination of PCBs is slightly less than with the common organochlorine pesticides. In several interlaboratory studies involving biological samples and paperboard containing either added Aroclors or actual residues of PCB the coefficients of variation are about ± 20 percent. The results of studies conducted by the AOAC and the FDA involving samples containing added Aroclors have been mentioned above (Food and Drug Administration, 1971; Burke, 1971; Food and Drug Administration, 1973; Sawyer, 1973); the recoveries of added Aroclors ranged from 74 to 101 percent and coefficients of variation from 9 to 15 percent. The levels of Aroclors added in these studies ranged from about 2 to 8 ppm with the exception of 0.2 ppm Aroclor 1254 added to chicken infant food. With samples containing actual residues, 9 laboratories in the AOAC study reported 9.2 ppm ± 8 percent for a residue in chicken fat and 4.5 ppm ± 20 percent for a residue in Lake Michigan chubs. The residue in the chubs was determined after separation of DDE, DDT, and TDE by column chromatography on silicic acid. In a study by 8 laboratories in cooperation with the International Council for the Exploration of the Sea, PCB residues determined in a fish oil averaged 1.97 ppm ± 47 percent. A much better coefficient of variation, about ± 11 percent, was obtained when the same fish oil was fortified with an additional 10 ppm PCB (International Council for Exploratoin of the Sea, 1974). In an AOAC study of the method for PCB in paperboard 11 laboratories analyzed a paperboard sample manufactured to contain Aroclor 1242 and reported 5.6 ppm ±

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16 percent (Finsterwalder, 1974). The inter- or intra-laboratory precision of the determination of PCB in any sample type is improved by use of the same analytical procedures, especially in quantitation of the residue.

The lower limit of quantitation for PCB residues will vary among laboratories depending upon the objectives of their analyses and upon the particular details of the analytical methods, especially the sensitivity of gas chromatographic detection and the sample size. The quantitation limit achieved will be higher than for organochlorine pesticides because of lower effective detector response to the technical PCB mixtures; 20-30 times more Aroclor 1254 or 30-50 times more Aroclor 1242 than DDE is required for the major peaks to produce the same peak height as DDE in electron capture gas chromatography (Food and Drug Administration, 1968-1975). Other factors which may restrict the attainment of low limits of quantitation and affect analytical reliability are interfering residues in the sample and laboratory contamination. Fish from some locations contain residues of organochlorine pesticides and possibly other contaminants at levels that would cause increasing difficulty as the PCB residue decreases below about one ppm. Contamination of laboratory equipment, reagents, and samples with PCB from containers, previous samples, control runs, and unknown sources, must be carefully guarded against in analyses where a low level of quantitation is necessary, for example with human blood or certain

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environmental samples (Trotter, 1975; Jensen et al., 1972; Giam and Wong, 1972). Perchlorination of the PCB residue to decachlorobiphenyl offers the possibility of about 25 fold increase in sensitivity in the gas chromatographic determination (Armour, 1973). However, contaminants present in antimony pentachloride severely restrict or prohibit application of this procedure to determination of low levels of PCBs (Trotter and Young, 1975). Analytical methods used by the FDA for PCB residues also recover chlorinated napthalenes (Armour and Burke, 1971). If present alone, chlorinated naphthalenes would be recognized by the analyst. However, their presence in admixture with PCBs would probably go unrecognized unless amounts were greater than PCBs or the residue was examined by mass spectrometry. Chlorinated naphthalenes are oxidized by procedures used to differentiate DDE in the presence of PCBs and could be removed from interfering in the PCB determination (Holmes and Walden, 1972).

From examination of procedures used to analyze for chlorinated dibenzofurans in commercial PCB formulations and from analytical studies with chlorinated dibenzodioxins it can be inferred that some chlorinated dibenzofurans may be recovered along with PCBs through analytical methods using Florisil and column chromatography (Vos, et al., 1970; Roach and Pomerantz, 1974; Bowes, et al., 1975; Porter and Burke, 1971). The chlorinated dibenzofurans have gas chromatographic properties similar to the PCBs (Bowes, 1975).

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It is very doubtful, however, that a relatively small amount of chlorinated dibenzofuran in the presence of PCBs would be recognized in the usual analysis for PCBs.

Little study has been made of residue analytical methodology for chlorobiphenylols (hydroxylated chlorinated biphenyls). Procedures used for their determination differ substantially from those used for PCBs (Bache and Lisk, 1973; Zitko et al., 1974). It is not likely that chlorobiphenylols would be recovered through column chromatographic and separation procedures used for PCBs.

In the discussion of PCB residues in foods given in the report of the Human Exposure Group a large share of the information comes from the FDA's surveillance programs. The analytical methodology used in the analyses is described in the FDA Pesticide Analytical Manual, Vol. I, and in Official Methods of Analysis of the AOAC. Quantitation of PCB residues is by gas chromatography with electron capture or halogen specific electrochemical detectors. The total response (area or peak height) for the PCB residue is compared to the total response for the Aroclor reference (or mixture of Aroclors) having the most similar gas chromatographic pattern. Aroclor reference materials are each from a single master lot. Results are reported as ppm of the Aroclor(s) used for the quantitation reference. With certain exceptions the limit of quantitation for PCBs (based on the electron capture detector response to Aroclor 1254) is

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about 0.2 ppm for individual foods and about 0.05 ppm for Total Diet composites. Fish from certain fresh water locations are the food most frequently and consistently found to contain PCB residues. The residues in fish are most often similar in gas chromatographic peak pattern to Aroclor 1254 but usually with higher concentrations of the late eluting (higher chlorination) chlorobiphenyl components.

E. Chlorinated Dibenzofurans

(See Appendix for structural information and definitions)

In considering the potential hazard to humans of the commercial chemical mixtures of chlorinated biphenyls called PCBs, one must consider which if any identified trace contaminant in these complex mixtures might contribute significantly to the overall hazard potential of the mixture. Although there is evidence for the presence of chlorinated napthalenes and possibly chlorinated terphenyls in PCBs, the chlorinated dibenzofuran (Cl-DBF) contaminants are regarded as a greater potential danger for several reasons. In using a chick bioassay to monitor fractionation of commercial PCB mixtrues, it was found (Vos et al., 1970) that the fraction most toxic to chicks, and far more toxic than the other fractions, contained Cl-DBFs and chlorinated naphthalenes. What limited toxicological information there is available on these halogenated naphthalenes, terphenyls and dibenzofurans suggests that only the Cl-DBFs may be more toxic than chlorinated biphenyls by orders of magnitude (Bauer et al., 1961; Moore et al., 1976).

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The extremely high toxicity of some of the chlorinated-dibenzo-p-dioxins (NIEHS Conference 1973; Schwetz, et al., 1973) a class of organic chemicals very similar in structure to the Cl-DBFs, also suggests the latter are likely to be highly toxic. Knowledge of the chemistry and toxicity of various chlorinated dibenzo-p-dioxin structures and the relationship between toxicity and structure, although recently developed, is more complete than for Cl-DBFs. Therefore, findings in the chlorodioxin field provide indicators to assess the difficulties likely to be encountered in the study of Cl-DBFs.

Chlorinated dibenzofuran contaminants have been reported and confirmed in PCB mixtures manufactured in Germany and France (Vos et al., 1970; Bowes, et al., 1975a) in Japan (Roach and Pomerantz, 1974a; Nagayama, et al. 1975) and in the United States (Aroclors) (Roach and Pomerantz, 1974b; Bowes, et al., 1975a). An additional claim that a cl-DBF contaminated an Aroclor was not sufficiently supported by the evidence presented (Curley et al., 1975). In the PCBs of U.S. manufacture, the range of Cl-DBFs found was from dichloro through hexachloro (see references cited above) and sufficient evidence was obtained to show that 2,3.7,8-tetrachloro and 2,3,4,7,8 -pentachlorodibenzofuran are presen' in Aroclors (Bowes et al., 1975b). That the Cl-DBFs reported were actual contaminants and not artifacts resulting from the experimental procedures used, was considered in two instances (Roach and Pomerantz, 1974b; Nagayama et al., 1975).

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Proper quantitation of the individual Cl-DBF contaminants is very difficult. It requires full structural identification of the Cl-DBF contaminant, availability of the contaminant as a highly purified reference standard for quantitation purposes and evaluation of the procedure used to concentrate and separate the Cl-DBFs, (e.g. from chlorobiphenyls) to determine the capability of the procedure to recover the specific Cl-DBFs in the PCB mixture. Reported attempts to quantitate the Cl-DBFs in PCB suggest contamination levels in the low parts per million range for total chlorinated dibenzofurans (Bowes et al., 1975a; Nagayama et al., 1975). Many of the reported values probably can be taken as minimal in the absence of recovery data.

Although the source of the Cl-DBF contaminants in commercial PCB mixtures has not been determined, several possibilities may be considered. The simplest explanation would be the likely presence of dibenzofuran (parent compound) in the technical grade biphenyl subjected to the chlorination process. From a consideration of the procedures used in the commercial synthesis of PCBs (Hubbard, 1964) various chlorinated biphenyls, if substituted in the ortho and ortho-prime positions with hydroxy groups and/or chlorine atoms, might ring close to form the furanoid ring by dehydration or dehydrochlorination.

It is important to recall that Cl-DBFs have been reported as contaminants also in other chemicals of commercial importance. Samples of pentachlorophenol (Schwetz et al., 1974) as well as

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lower chlorinated phenols (Firestone et al., 1972) and hexachlorobenzene, (Villanueva et al., 1974) have been found to contain a range of Cl-DBFs. The ppm level of Cl-DBFs in certain pentachlorophenols examined by Schwetz and co-workers (1974) was considerably higher than the highest level thus far reported in commercial PCB mixtures; the chlorine level in the reported dibenzofuran contaminants of pentachlorophenol ranged from hexa to octa.

It is now known that "PCB residues" obtained from environmental samples usually do not simply represent an easily identified original commercial PCB mixture. For example, there is evidence from the study of electron capture gas chromatograms that certain chlorinated biphenyl compounds are preferentially lost or concentrated in passing through environmental media. This has led to recent studies of the toxicity, metabolism and physiological effects of specific, individual chlorinated biphenyl compounds, synthesized by routes intended to yield a single compound of known structure. In addition to permitting the development of structure-activity correlations, these studies presumably were intended to avoid complications in interpreting results from the testing of the commercial chlorinated biphenyl mixtures (Vos and Notenboom-Ram, 1972), now known to contain toxic Cl-DBFs as contaminants. Interpretaion of results from the testing of individual chlorinated biphenyl compounds, however, may not be entirely straight forward. In the Ullmann coupling reaction of

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2,4,5-trichloroiodobenzene, it has been reported that the highly toxic 2,3,7,8-tetrachlorodibenzofuran is formed in 3% yield in addition to the expected 2,2'4,4',5,5'-hexachlorobiphenyl product (Moron, et al., 1973). This hexachlorobiphenyl is a significant constituent of PCB mixtures (Sissons and Elti, 1971; Tas and Kleipool, 1972; Jensen and Sundström, 1974) and has been singled out for biological studies by several workers (Vos and Notenboom-Ram, 1972; Johnstone et al., 1974; Hansell and Ecobichon, 1974). Careful purification and, if necessary, chemical analysis of symmetrical chlorobiphenyls prepared by the Ullmann coupling reaction (for dibenzofuran content) is suggested as a prerequisite to biological testing of the biphenyl.

There are two other aspects of the chemical relationship betwen chlorinated biphenyls and Cl-DBFs that need to be mentioned. Both deal with possible environmental alteration. Evidence has been obtained for photochemical conversion of certain chlorinated biphenyls to Cl-DBFs in very low yields (Crosby and Moilanen, 1973). Although the scope of this study was limited, formation of Cl-DBF was shown to occur under conditions of sunlight irradiation and in the laboratory using sunlight-simulating conditions. Two different ortho-chlorinated biphenyls (the 2,5-dichloro and 2,2',5,5'-tetrachloro) were claimed to produce approximately 0.2% steady-state yields of a monochloro DBF. The limited reports regarding the photochemical decomposition of Cl-DBFs (Crosby and Moilanen, 1973; Hutzinger et al., 1973) indicate relatively

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rapid destruction of the compounds may take place in the environment. Since reductive dechlorination is a major route of photochemical alteration of Cl-DBFs, the possibility of dechlorination of highly chlorinated DBFs to more toxic DBFs of lower chlorine content must be considered. The extent to which specific chlorinated biphenyls, found as major constituents of commercial PCB mixtures, can be photochemically converted to Cl-DBFs can only be determined by further experimental studies.

Analysis of the Yusho oil (the rice oil contaminated by PCB-containing heat exchange fluid implicated in the Japanese "Yusho" poisoning incident) by Nagayama et al., (1975) for Cl-DBF content, led to a value of 5 ppm Cl-DBFs. This value is about 300 times the Cl-DBF level expected in the Yusho oil if one simply assumes contamination of the oil by Cl-DBFs to be proportional to the Cl-DBF level found in unused Kanechlor 400 (the Japanese PCB mixture claimed to have been used as the heat exchange fluid) and to the level of PCB in the Yusho oil. This led Kuratsune et al., (1975) to suggest that Cl-DBF levels increased in the heat exchange fluid through use. Going a step further, these questions may be raised: Is Cl-DBF concentration increased, generally, in PCB-containing heat exchange fluids through use? Does such increase occur in PCB-containing transformer fluids or electrical capacitors through use?

A critical review is needed of the published data upon which Kuratsune's suggestion is based (Nagayama et al., 1975), particularly

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since the results from a recent analysis of a portion of Yusho oil (Trotter, 1976) raises questions about the concentration of chlorinated biphenyls in the Yusho oil. Further laboratory studies suggested by such a review and analyses of selected, used PCB-containing industrial fluids might help to answer the above questions.

Considering the Cl-DBFs as the toxicologically most significant class of chemical impurities in the PCB mixtures, the questions may be asked: what portion of the observed effects from animal and human exposure to PCB mixtures can be attributed to the Cl-DBFs? It is doubtful this question can be answered in any quantitatively explicit way. There are analytical problems in identifying and measuring accurately the amounts of chlorinated dibenzofurans in various PCB mixtures. Even though only a relatively few of the 135 possible chlorinated dibenzofurans may be identified in PCB mixtures, the toxicity of these compounds can be expected to vary with both number and ring position of chlorine atoms in the Cl-DBF molecule. Toxicity data on specific, high purity Cl-DBFs is very limited because the compounds themselves are not readily available. In addition to these, essentially chemical, difficulties, toxicological judgements would be difficult to make. To begin to evaluate the toxicological "burden" to be placed on Cl-DBF contaminants in commercial PCB mixtures, a practical approach would be to use analytical procedures that can recover and quantitate specific Cl-DBF compounds known to be highly toxic. For example, 2,3,7,8-tetrachlorodibenzofuran, already reported by Bowes (1975b) as

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present in PCBs, can serve as a measure of potential hazard until further toxicity data for Cl-DBFs become available.

To date, there have been no published, positive findings of Cl-DBFs in environmental samples or in foods. Analytical procedures to detect Cl-DBFs in such samples should be developed, tested and applied to appropriate samples. If chlorinated dibenzo-p-dioxin residue analytical findings can be taken as an indicator, procedures suitable for parts per trillion detection of Cl-DBFs will be required and quantitation will be difficult.

No clear evidence for the presence of chlorinated dibenzo-p-dioxins in commercial PCB mixtures has been reported. A recent publication suggesting the presence of such contaminants in some PCBs and in a synthesized chlorinated biphenyl (Ax and Hansen, 1975) almost certainly misinterpreted the significance of the experimental finding related to the dioxins.

III. Chemistry of Brominated Biphenyls

A. Comparison of Brominated Biphenyls with Chlorinated Biphenyls

Unlike PCBs, the chemistry and stability of PBBs have not been well studied and documented in the literature. It is difficult to assess the stability and the extent of possible chemical conversion of PBBs in the environment. PBBs can be compared chemically to the PCBs. Since both bromine and chlorine are

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halogens, PBB and PCB chemistry should be similar in some respects. Bromine, however, is a better leaving group in chemical reactions than chlorine. The described laboratory experiments concerning PBB alkaline hydrolysis and photolysis show that bromine is more labile than chlorine under comparable reaction parameters. PBBs may, therefore, be less stable in the environment if PBBs were under the same physical reaction parameters in the environment as PCBs. The physical state and other physical reaction parameters of PBB and PCB residues in the environment can determine reactivity. Liquids and vapors often react more readily than solids. Aroclors are liquids, though some Aroclors are extremely viscous at room temperature. Some PCBs, especially the lower chlorinated components, are volatile. FireMaster BP-6, however, is a solid and has an extremely low vapor pressure. The production, distribution, and usage of PBBs has not been as wide spread as PCBs. PBBs, unlike PCBs, may not be physically located in a position for chemical reaction. FireMaster BP-6 has been extensively used, for example, in thermoplastics, such as typewriter and business machine housings (Kerst, 1974). FireMaster BP-6 has little tendency to migrate from the thermoplastic into which it is incorporated. The major portion of the products into which FireMaster BP-6 is incorporated is assumed to be buried eventually in refuse dumps. PCBs, on the other hand, are often used in transformers and capacitors and can be exposed to high temperatures which can accelerate possible chemical reactions. PCB residues are found in many diverse locations

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throughout most of the world. Many of these locations may offer conducive settings for chemical and metabolic conversions. PCB residues in a body of water may react photolytically, whereas PBB residues buried in a refuse dump would not be in a position to absorb light.

B. Non-metabolic Alteration of Brominated Biphenyls

Oxidation and Hydrolysis

The stability of PBBs to oxidation has not been studied and documented in the literature. FireMaster BP-6 is unstable to alkaline hydrolysis. After refluxing FireMaster BP-6 with 2% KOH in ethanol, GLC chromatograms show erratic degradation of hexabromobiphenyl (DET,DO,DCT,DCH,1976), the major component of FireMaster BP-6. The possible rate of PBB hydrolysis in the environment under milder conditions is not known.

Photochemistry

Recent analysis of FireMaster BP-6 by GCMS using an OV 101 column demonstrated 12 peaks whose mass spectrum corresponds to 2 pentas, 4 hexas, 4 heptas and 2 octas. However, about 50 percent of the material is 1 hexa isomer with the next most abundant component being the hepta isomer at about 20-25 percent. Nuclear magnetic resonance and chemical studies have identified the principal component of Firemaster BP-6 as 2,2'4,4'5,5'-hexa-bromobiphenyl (Anderson et al., 1974; Sundström et al., 1976).

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The photolytic rates of reactivity of FireMaster BP-6 and 2,2'4,4'5,5'-hexachlorobiphenyl in methanol solutions irradiated with 3000 Å light were compared (Ruzo and Zabik, 1975). The rate of reaction of FireMaster BP-6 was determined presumably by the decrease in the GLC peak of hexabromobipenyl. Hexabromobiphenyl was found to be seven times as reactive as the corresponding PCB. Hexabromobiphenyl was found to undergo photolytic reductive debromination in methanol yielding penta- and tetrabromobiphenyls and also > 1% methoxylated product. Dimethoxy tetrabromobiphenyl was identified as a product by mass spectrometry. The highly efficient photoreactivity of PBB may be due to: 1. enhanced intersystem crossing to a triplet state due to vibronic coupling with the bromines, 2. steric interference due to the bromines, and 3. the relatively low carbon-bromine bond energy. The aromatic carbon-bromine bond energy is 71 kcal/mole vs the aromatic carbon-chlorine bond energy of 86 kcal/mole (Kerst, 1974). As with PCBs (Ruzo, et al., 1974), presumably ortho halogens preferentially cleave in PBBs upon photoexcitation.

The possible rates and extent of photolytic reactivity of PBBs in the environment are not known. The photochemistry of PBBs has not been studied in the vapor or solid states. Since FireMaster BP-6 has an extremely low vapor pressure, vapor state photochemistry in the environment would be extremely limited. The extent of thin film PBB photochemistry in the environment may also be limited. PBB contamination and resulting

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photochemistry in river waters, except in the vicinity of PBB production facilities, may be limited. PBBs incorporated into thermoplastics, which are presumably buried eventually in a refuse dump, are not likely to absorb much light for photolytic reaction.

C. Brominated Biphenyls: Determination of Residues

Polybrominated biphenyl (PBB) residues are analyzed for in foods by methods quite similar to those used for organochlorine pesticides and polychlorinated biphenyls (PCBs) (Food and Drug Administration, 1968-1975; Fehringer, 1975; Food and Drug Administration, 1976). Recoveries of PBB added to samples in vivo through these procedures is over 80 percent. A method to improve extraction efficiency of PBB residue from dry, high fat animal feeds has been reported (Fehringer, 1975).

The major difference from methods for organochlorine pesticides is in the gas chromatographic determination which is done at higher temperatures or on columns with low liquid phase loads because of the lower volatility of PBBs. Methyl silicones or Silar-10C, the liquid phases most frequently used, separate the technical PBB, FireMaster BP-6, into 3-9 peaks depending on the chromatographic conditions selected. PCBs and organochlorine pesticides which would be recovered through extraction and cleanup procedures together with PBBs have earlier retention times under these conditions and are separated from the

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major PBB constituent, hexabromobiphenyl. The retention times of hexabromobiphenyl and decachlorobiphenyl are not greatly different on methyl silicone liquid phases but are widely separated on Silar-10C. Elution of the Florisil column used for cleanup of extracts with petroleum ether rather than a mixture of petroleum ether and ethyl ether separates PBBs from most organochlorine pesticides prior to gas chromatography and improves cleanup for the PBB determination.

PBB residues are detected and quantitated with the electron capture gas chromatography detector. Quantitation is based on comparison of the size of the hexabromobiphenyl peak in the residue to the size of the hexabromobiphenyl peak in a known weight of the reference material, FireMaster BP-6. FireMaster BP-6 is a technical mixture containing 60-70 percent hexabromobiphenyls (Sundström and Hutzinger, 1976). The accuracy of residue quantitation is affected by any change in the composition of the residue from that of the reference technical PBB mixture. The identity of PBB residues can be confirmed by thin layer chromatography, photochemical alteration, halogen-specific gas chromatographic detection, and by different retention times on Silar-10C and methyl silicon gas chromatographic columns (Food and Drug Administration, 1976; Fehringer, 1974; Fehringer, 1975; Erney, 1975). Mass spectrometry has also been used to confirm the identity of the PBB residue (Ayers, 1975).

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The limit of quantitation for PBB residues, including capability for residue identity confirmation, is about 0.05 ppm in fats and 0.01 ppm in non-fats (Food and Drug Administration, 1976). Formalized interlaboratory studies have not been reported for analytical methods for determination of PBB residues.

D. Possibility of Brominated Dibenzofurans in Commercial PBB Mixtures

There has been no report, so far, of the finding of brominated dibenzofuran (Br-DBF) compounds in commercial PBB mixtures. Examination of FireMaster BP-6 for possible contamination by Br-DBF is in progress in several laboratories.

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METABOLISM AND BIOCHEMICAL TOXICITY OF PCBs and PBBs

I. Effects of PCBs on Biochemical Functions

One of the major biochemical effects of PCBs is the induction of microsomal enzymes in the liver. Risebrough et al., (1968) suggested that PCBs had the capability to induce the activities of microsomal enzymes. Subsequently, Street et al., (1969) demonstrated the induction of liver enzymes in rats by PCB's. Since then, a great number of articles have been published on this subject.

The enzyme systems studied have included mainly hydroxylases, N- and O-demethylases and nitroreductases, and to a lesser extent nonspecific carboxylesterase, bromosulphophthalein-glutathione conjugating enzyme, p-nitrophenol UDP-glucuronyl transferase and EPN-detoxification systems.

The induction of microsomal enzymes by commercial PCBs has been demonstrated perorally in rabbits (Villeneuve et al., (1971), rats (Litterst et al., 1972a) and primates Allen et al., 1974) and via intraperitoneal injection (Bickers et al., 1972) and skin application in rats (Bickers et al., 1975). Values reported for the threshold of enzyme induction by PCB's vary between 0.5-25 ppm. (Litterst et al., 1972b; Villeneuve et al., 1971; Turner et al., 1974).

The time-course of microsomal eyzyme induction was studied by Litterst et al., (1974) in rats. They found that significant levels of enzyme induction occurred after 7 days of feeding PCBs

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in the diet. A single oral dose in rats resulted in maximum enzyme activities at 24 hours. Bickets et al., (1974); 1975) have shown that maximum induction occurred within 2-6 days in rats after cutaneous exposure to Aroclor 1254 or microscope immersion oils containing 30-45% chlorine.

In order to study the effect of chlorine content of PCB's on enzyme induction, different commercial PCBs were investigated. Litterst et al., (1972b) studied PCBs with chlorine contents from 42 to 60%. In rats the maximum activity of demethylase was observed with the 54% chlorine PCB's; maximum activity for nitroreductase was obtained with the 60% chlorine PCBs. Chen et al., (1973) reported that 54% chlorinated PCBs gave maximum response of demethylase in rats. Similar results were reported by intraperitoneal injection of various PCBs in rats (Ecobichon et al., 1974). Goldstein et al., (1975) and Iverson et al., (1975) studied the effects of Aroclor 1016 and Aroclor 1242 on enzyme induction in rats. Both PCBs have approximately 42% chlorine, but the content of the penta-, hexa-, and hepta-chlorine isomers of Aroclor 1016 is reduced to 10% of that in Aroclor 1242. Their results showed that Aroclor 1242 was a much more potent inducer than Aroclor 1016 in female rats. In comparing Aroclor 1232, ~~Aro~~clor 1248 and Aroclor 1260, Schmoldt et al., (1974) found that Aroclor 1260 was the most potent enzyme inducer in rats.

The synthetic and isomerically pure PCBs have been investigated for enzyme induction, Chen et al., 91973b) found that both

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2,3,4,5- and 3,5,3',5'-tetrachlorobiphenyls induced enzyme systems in male rats, but no significant differences were found between the two isomers. Johnstone et al., (1974); Ecobichon et al., (1975); Ecobichon (1975) compared the effects of position of chlorine atoms on the ring. They found that enhanced induction of mono-oxygenases was observed for PCBs having chlorine atoms substituted at the 4- and 4'- positions irrespective of chlorination at other positions. Substitution at the 2-position was next in importance followed by substitution at the 3-position. They concluded that the position of chlorination was as important as the degree of chlorination.

There are two types of enzyme inducers being reported in the literature. One group to which phenobarbital belongs resulted in increased cytochrome P-450 content, as well as increased benzpyrene hydroxylase and ethylmorphine demethylase activities in the liver. The second group includes polycyclic hydrocarbons. This group stimulates the formation of cytochrome P-448 and an increase in hydroxylation but not demethylation. Alvares et al., (1973) reported that rats treated with PCBs produced an increase in cytochrome P-448, hydroxylase, as well as demethylase. Therefore, it appears that PCBs display induction behavior typical of both groups.

Most of the enzyme induction studies were evaluated in vitro. Several workers indeed have observed enzyme induction effects in vivo by demonstrating shortened barbiturate sleeping times (Bickers et al., 1972; Johnstone et al., 1974; Villeneuve et al., 1972):

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Commercial PCBs are known to contain small amounts of dibenzofurans (DBF). DBFs were found to be 170 times as potent as PCBs in inducing enzymes.

Alvales & Kappas (1975) reported the induction of hydroxylase and demethylase in placenta, as well as in the fetus, when pregnant rats were treated with PCBs Vainio (1974) reported that Clophen A50 enhanced hydroxylase 5-fold in the lung and 8-fold in the kidney microsomes, whereas the microsomes from duodenal mucosa exhibited no enhancement. Benzpyrene hydroxylase activity in skin was also increased by PCBs (Bickers et al., 1975).

Vos and Koeman (1970) found that several tissues of PCB-treated chickens were strongly fluorescent under ultra violet light. They suggest that PCBs could induce chemical porphyria in chickens. Later, they demonstrated that mitochondrial ALA Synthetase activity increased 20-fold and fecal porphyrin levels were significantly increased in Japanese quail treated with PCBs (Vos, 1971; Vos et al., (1972). They suggested that the porphyria caused by PCBs is due to the increase of ALA synthetase, followed by overproduction of porphyrins. Similar results in rats were obtained by Goldstein et al., (1974), and Bruckner et al., (1974). Goldstein et al., (1974) suggested that the induction of ALA synthetase is probably not the primary cause of PCB-induced porphyria because of the delayed onset of porphyria as compared with ALA synthetase induction. They suggest that the ALA synthetase in the liver may be related to the increase of cytochrome P-450 content. This

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idea was supported by Grote et al., (1975). Aroclor 1242 was found to be a more potent inducer of liver porphyria than Aroclor 1016 (Goldstein et al., 1975). Both Aroclors have similar chlorine content, but Aroclor 1242 contains 9% homologs with five or more chlorines while Aroclor 1016 contains only 1% of such homologs. Sinclair and Granick (1974) showed that cultured liver cells respond rapidly to PCBs in accumulation of uroporphyrin. Simon et al., (1974) suggested that porphyria may be due to the destruction of the phospholipid structure of cell membrane, resulting in increased permeability of the substrate. Hirayama et al., (1974) observed hypo-bilirubinaemia in Yusho patients and suggested that the induction of bilirubin UDP-glucuronyltransferase may be responsible for the low plasma bilirubin content. However, recently Bastomsky et al., (1975) showed that the lowering of serum bilirubin concentration by PCBs is due to the reduced binding of bilirubin to plasma protein rther than to the enzyme induction. Wit (1972) has shown that PBBs which are similar to PCBs are potent hepto-porphy-rinogenic chemicals.

The chemical and structural similarity of DDT to PCBs led Jefferies et al., (1972) to study the effects of PCBs on thyroid functions. They found an increase in thyroid weight in PCB-treated black-backed gulls as compared to controls. Hurst et al., (1974) found no clear-cut effect of PCBs on thyroid gland size in quails. Byrne et al., (1975) reported that PCBs increased

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thyroxine levels in the blood and also promoted peripheral degradation of thyroxine in female minks. Bastomsky (1974) found a 4 to 5-fold increase of biliary excretion of thyroxine in rats treated with PCBs. PCBs also elevated iodine uptake by the thyroid and reduced serum PBI concentration. Recently Bastomsky and Wise, (1975) showed similar results in rats due to either intraperitoneal injection or skin application of microscope immersion oil. Walker (1975) found that inclusion of Aroclor 1254 in fish food resulted in an increase in fish thyroid activity.

The effects of PCBs on ATPase and oxidative phosphorylation have been examined by a number of investigators. $Na^{+}K^{+}$-ATPase and Mg^{++} ATPase from several fish tissues were found to be inhibited by PCBs. (Yap et al., 1971; Cutkomp et al., 1972; Desaiah et al., 1972; Koch et al., (1972). Further study showed that in vitro data were not in agreement with the in vivo data (Yap et al., (197a). The inhibition of ATPase in fishes by PCBs was also reported by Kinter et al., (1972) and by Davis et al., (1972).

Sivalingan et al., (1973) investigated the effects of PCB on the oxidative phosphorylation of rat liver mitochondria. They showed that the mode of inhibition appears to be different with PCBs of different chlorine content. PCBs with low chlorine content inhibited energy and electron transfer but PCBs with high chlorine content not only inhibited energy and electron transfer but also had an uncoupling effect. LaRocca et al.,

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(1975) showed that the administration of commercial PCBs, as well as purified isomers to rats inhibited the total ATPase activity in liver, kidney and brain tissues.

Pardini (1971) has demonstrated that a marked inhibition of respiratory enzyme systems occurred when heavy beef heart mitochondria were exposed in vitro to numerous PCBs. Chesney and Allen (1974) showed that the addition of PCBs to rat liver mitochondria in vitro caused an inhibition of oxidative phosphorylation and respiration. Feeding rats with PCBs at the 1000 ppm level increased the oxidative phosphorylation in liver mitochondria, however no effect was seen at the 100 ppm level.

Sharp et al., (1974) reported that the inhibition of beef brain and rabbit kidney $Na^{+}K^{+}$-ATPases can be reversed or prevented by phosphatidylserine or phosphatidylinositol, but not by phosphatidychloline and phosphatidylethanolamine. They suggested that acidic phospholipids are required to stabilize the enzyme and thereby overcome the effect of PCBs.

Risebrough et al., (1968) suggested that PCBs had the capacity to enhance steroid-hydroxylating enzyme activity, thus affecting estradiol metabolism. In addition, certain low chlorine containing PCBs have estrogenic activity which is reflected by an increase in glycogen content of the uterus of immature rats (Bitman and Cecil, 1970). Similar results were obtained by Fumiko (1972) in rats (Bitman and Cecil, 1970). Similar results were obtained by

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Fumiko (1972) in rats and by Orberg, and Kihlstrom (197) in mice. Orberg et al., (1972) found that the estrous cycle of the mouse increased in length after a single injection of PCBs. Lincer and Peakall, (1973) reported an increased rate of metabolism of estradiol in vitro in the liver of American kestrels after the feeding of PCBs. Similar results were also reported in white leghorn cockerels and pullets (Nowicki and Norman 1972). Platonow and Funnell (1971) demonstrated that feeding PCBs to cockerels resulted in a decrease in testicular and comb growth. Decreased urinary excretions of estrogen and dehydroepiandrosterone were also observed in cockerels when PCBs were administered in high doses (Platonow et al., 1972). Ecobichon and Mackenzie, (1974) studied the uterotropic activity of commercial and isomerically pure PCBs in rats. They found significant changes with a number of PCB mixtures but experiments with the isomerically pure PCBs were inconclusive. Changes were observed with 2-chloro and 2,2-chlorobiphenyls. Nelson (1974) reported that PCBs are effective inhibitors of the binding of ^{3}H-estradiol to the rat uterus cytosol fraction in vitro. Recent data showed that PCB feeding caused neither significant chromosomal damage nor arrest in the rate of spermatogenesis in male rats (Dikshith et al., (1975).

Flick et al., (1965) noted enlarged adrenals and small spleens in PCB-treated white leghorn cockerels. Wassermann and Wassermann (1972) and Wessermann et al., (1973) reported that rats receiving 200 ppm PCBs showed an increase in plasma corticosterone levels.

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These changes were concimitant with morphological changes in the zona fasciculata of the adrenal gland which indicated increased activity. Sanders, et al., (1974) have shown similar increases in serum corticosterone in mice fed 60 to 1000 ppm PCBs.

It is known that DDT decreases the utilization of dietary carotene and liver storage of vitamin A in rats and cattle (Phillips, 1963; Phillips, and Hidiroglou, 1965). Villeneuve et al., 1971) reported that Aroclor 1254 but not Aroclor 1221 reduced the liver concentration of vitamin A in pregnant rabbits. Decreased liver vitamin A concentrations were found in male and female rats and also Japanese quail after PCB feeding (Cecil et al., 1973). However, the laying female quail did not appear to be affected.

The effects of PCBs on vitamin E have been studied by Combs et al., (1975). Their results indicated that dietary PCBs increased the incidence of exudative diathesis in chicks and that this increase can be overcome by increasing dietary vitamin E or selenium. The vitamin D mediated calcium metabolism was found to be altered by the oral administration of PCBs to chickens (Wong et al., 1974).

II. The Comparative Biochemical Toxicity of Aroclor 1254 and Firemaster BP-6

PCB's have been reported to affect a large number of biochemical systems. To the extent that it has been reported, PBBs

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affect most of these same systems in a similar fashion. However, quantitative and possibly qualitative differences do not appear to exist in the response of some biological parameters. These include thyroid hyperplasia (Norris et al., 1973) and microsomal enzyme induction (Farber and Baker, 1970).

A preliminary study was conducted to compare the relative effect of Aroclor 1254 (Aro) with Firemaster BP-6 (FM) (Garthoff et al., 1975). This was set up as a broad survey to give an estimate of the relative biological activity of these chemicals in may different systems and pin point areas where further more definitive work should be done.

Table 1 summarizes the time sequence of the various parameters studied. Adult male rats were fed either 0, 5, 50, or 500 ppm Aroclor 1254 or Firemaster BP-6, mixed in the diet, for 2, 3, or 5 weeks.

Due to the large number of parameters examined and the time restraints placed on the study, the experimental design did not permit a totally unambiguous comparison between all of the effects caused by Aro and FM. Some apparent differences in biochemical responses determined at sacrifice may have been partly due to the fact that, for the three-week study, rats were exposed to FM for 48 hours longer than rats were exposed to Aro. Although it is felt that under the experimental conditions, this effect should be small, critical comparison of Aro and FM toxicity should be

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considered tentative until smaller experiments are conducted which can eliminate this difference in exposure time. The following evaluations were made based on the assumption that this two day difference had no effect.

Some parameters showed no consistent or dose related change with either chemical at any level. These included relative kidney weight and testes weight, hematology, SGPT, SGOT, plasma BUN, plasma corticosterone, the rate of liver protein synthesis per g tissue, liver dry weight, lyophilizable kidney, liver, or testes, the incidence of chromosome abnormalities and the number of cells in mitosis from bone marrow of spermatogenial cells.

Growth and adipose tissue weight were equally depressed by Aro and FM when fed over a three week period at 500 ppm. The growth effect appeared to be due primarily to decreased food efficiency.

Three parameters were more sensitive to Aro than to Fm. These included the decreased liver protein and liver RNA per g tissue and the decreased plasma glucose.

On the other hand, six parameters were more sensitive to FM. These included liver growth, increased liver lipid (total lipid, cholesterol, phospholipid, and neutral lipid), elevated plasma cholesterol, increased microsomal enzyme activities, impaired mitochondrial function, and decreased liver RNA synthesis.

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Disruptions of the redox and energy states of the cell were produced by dietary exposure to Aro or FM. These effects were indicated by studies wit isolated mitochondria and frozen clamped liver. In the latter case the concentrations of adenine nucleotides, pyridine nucleotides, and glycolytic intermediates were determined. On a molar basis, hexabromobiphenyl was reported to be about five times more potent than Arochlor 1254 in causing some increased microsomal enzyme activities (Farber and Baker, 1974). A three-fold difference was observed between Firemaster BP-6 and Arochlor 1254 (Table 3).

A pathology team autopsied rats after both three and five weeks exposure to Aro and FM (Kasza et al., 1975). Pathological analysis of the liver of rats fed Aro or FM for three weeks showed no abnormalities on gross observation. No histopathological lesions were seen in controls, Aro groups, or the 5 and 50 ppm FM groups, after three weeks. In the 500 ppm FM group, minimal vacuolation and focal hepatitis were each seen in one rat. After five weeks exposure, gross observation of the liver indicated an increasing incidence of enlargement, friability, and prominent lobular pattern with increasing dose of both chemicals. Microscopically the 5 ppb Aro group appeared normal while 2/7 rats fed 5 ppm FM had minimal cytoplasmic degeneration. All rats had this lesion at 50 and 500 ppm Aro or FM, with increasing cellular lipid. This lesion was recent, centrilobular and coalescing with no change in fibrous tissue or glycogen. The histopathology was qualitatively similar but slightly more severe in rats fed FM

than in those fed Aro and is consistent with biochemical findings. The biochemical findings were all made after three weeks exposure at which time histopathological changes were not evident. Even at five weeks the histopathology was not severe enough to alter most of the clinical chemistry in the rat.

In most parameters evaluated, FM either caused an effect at a lower dose level or caused an effect in a shorter time or caused a greater effect at the same dose level, expressed as ppm in the diet, as Aro. When expressed on a molar basis FM becomes even more effective than PCB. Exceptions to this observation were noted at the 500 ppm dose level where differential effects of Aro and Fm were often eliminated.

A summary of the major effects seen are found in Tables 2, 3, and 4. In all but one case the maximum response of a parameter occurred at the highest dose level. Microsomal enzyme activities were, in general, greater at the 50 ppm level and the decline at 500 ppm relative to the 50 ppm level was more marked with FM.

III. Metabolism of PCB and PBB Mixture

Generally, the tissues from animals and man containing PCB from environmental exposure have GLC patterns resembling those of PCB mixtures with more than 50% chlorination. This is in marked contrast to the major manufactured products that generally contain 42% or less chlorine. While one cannot rule out the possiblity that differential uses favored introduction of more highly

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TABLE 1

PARAMETERS EVALUATED IN STUDY

EXPOSURE TIME

(WEEKS)

PARAMETERS	TWO	THREE	FIVE
Body weight	x	x	x
Liver weight	x	x	x
Other tissue weights		x	
Mitochondrial respiration	x		
Liver composition		x	
Liver protein synthesis		x	
Liver RNA synthesis		x	
Liver Microsomal enzyme activities		x	
Liver intermediary metabolites		x	
Serum cholesterol		x	
Serum enzymes		x	x
Plasma corticosterone		x	
Plasma protein		x	
BUN		x	x
Gross pathology		x	x
Histopathology		x	x
Cytogenetic analysis			x

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TABLE 2

RELATIVE BIOCHEMICAL RESPONSE TO Aro AND FM AFTER TWO WEEKS DIETARY EXPOSURE

	LEL[1] ppm		Maximum Effect % Control	
	Aro	FM	Aro	FM
PARAMETERS				
Liver weight / Body weight	500	50	170	183
Mitochondrial respiration	500	500	152	192

[1]LEL = lowest effective level that showed a dose-response relationship.

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TABLE 3

RELATIVE BIOCHEMICAL RESPONSE TO Aro AND FM
AFTER THREE WEEKS DIETARY EXPOSURE

	LEL[1] ppm		Maximum Effect % Control	
	Aro	FM	Aro	FM
PARAMETERS				
Body weight gain	50	500	52	52
Liver weight / Body weight	50	50	203	214
Liver dry wt.	NE[3]	50	NE[3]	107
Liver lipid	50	5	138	156
Liver cholesterol	500	50	226	232
Liver protein	500	NE	84	NE
Liver RNA	5	50	79	84
Liver DNA	5	5	58	60
Liver RNA snythesis	500	5	78	86

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TABLE 3 (Cont'd)

PARAMETERS	LEL[1] ppm Aro	LEL[1] ppm FM	Maximum Effect % Control Aro	Maximum Effect % Control FM
para-Nitrobenzoate reductase activity	50	5	288[2]	520[2]
Plasma glucose	50	NE[3]	79	NE[3]
Plasma cholesterol	500	5	178	256

[1]Lowest effective level that shows a dose response relationship.

[2]Maximum effect occurred at 50 ppm dose.

[3]NE = No effect

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TABLE 4

RESPONSE OF RELATIVE LIVER WEIGHT TO Aro AND FM AFTER FIVE WEEKS DIETARY EXPOSURE*

PARAMETER	LEL ppm		Maximum Effect % Control	
	Aro	FM	Aro	FM
Liver weight / body weight	500	50	171	216

* Legend - see Table 3.

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chlorinated materials in the environment, the observation has led to the general belief that the less chlorinated components are more readily metabolized.

The environmental observations have been confirmed in a large number of experimental feeding studies in a number of mammalian and avian species. The absence or diminished concentration of the early eluting peaks have been reported in rats (Grant et al., 1971a, Curley et al., 1971), rabbit (Grant et al., 1971b), cow (Fries et al., 1973a), quail (Bailey and Bunyan, 1972), and hens (Fries et al., 1973b).

The peaks not present in tissues and products generally are the early eluting peaks that correspond to the PCBs with lower degrees of chlorination. The observations are consistent with the belief that the rate of metabolic attack on PCBs decreases with increasing chlorination. Studies of the single PCB homologs of various degrees of chlorination have shown that those with five or less chlorine atoms are more radily metabolized and excreted than the PCBs with higher chlorination (Berlin et al., 1975; Hutzinger et al., 1972; Melvas and Brandt, 1973). The position of chlorine substitution also affects the retention and elimination of single homologs (de Freitas and Norstrom, 1974). Metabolism of individual PCBs will be discussed more thoroughly in another section.

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Among the various food species there appears to be one exception to the general rule that the less chlorinated PCBs are hydroxylated. The PCB residues in fish closely resemble the PCB to which the fish was exposed. There was little change in the relative concentrations of the various homologs (Stalling and Mayer, 1972). Consistant with this observation it has been found that mono-, di-, and tetrachlorobiphenyls are not metabolized by trout (Hutzinger et al, 1972).

Among the food producing animals (cattle, chickens) concentrations of PCB residues in milk and eggs reach a "steady state" after approximately 8 to 12 weeks of continuous intake (Fries et al., 1973a; Fries et al., 1973b). The ratio of residue levels in food products to levels in the animal's diet are greatest with PCBs of 54% chlorination. The residue levels in milk are approximately 4 times the residue level in the cow's diet. In hens, residue levels in eggs are approximately equal to the diet while residue level in the body tissue (fat basis) is approximately 6 times the dietary level. The ratio of residue level in product and tissues to intake is lower with PCBs of greater than 54% chlorination. Since it is unlikely that there is greater metabolism of the most highly chlorinated PCBs, the results suggest that the absorption for the GI tract is lower for the more highly chlorinated PCBs (Smith et al., 1976). PCBs of four or fewer chlorines rarely occur in animal products when the animals are fed environmentally realistic levels.

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Much less is known about the metabolism of PBB than PCBs. However, the observations that have been reported tend to be consistent with the reports on PCB metabolism.

While the PBB of most immediate concern for human health (BP-6, Michigan Chemical Co.) is a multicomponent mixture like the PCBs, it is much simpler than the ordinary commercial PCB mixtures. The major component is a single hexabromobiphenyl accounting for over 60% of the total material. The only other component occurring in significant amounts is a single heptabromobiphenyl.

In general, the measures of retention in edible tissues and excretion in edible products are similar for the hexabromobiphenyl and the hexachlorobiphenyls (Fries et al., 1976; Fries and Marrow, 1975). Heptabromobiphenyl retention and excretion is only 1/10 of that of the hexabromobiphenyl. In cattle that have been heavily contaminated with BP-6, the heptabromobiphenyl was barely detectable (milk or tissues) 6 to 8 months after the time of ingestion even though the hexabromobiphenyl level was over 1000 ppm (Fries et al., 1975). Since the heptabromobiphenyl is not more likely to be metabolized by the animal than the hexabromobiphenyl, it is reasonable to assume that its absorption is lower or its elimination through bile is greater than the hexabromobiphenyl component. Over 60% of octabromobiphenyl is excreted in the feces as the parent compound when it is fed to rats (Norris et al., 1974). This observation supports the conclusion that there is less absorption with increasing halogenation.

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IV. The Metabolism of Individual PCBs

Quantitative studies of the distribution of PCBs indicate that most, if not all, PCBs which contain six or fewer chlorine atoms are efficiently abosrbed from the gut of higher animals (Albro and Fishbein, 1972; Matthews and Anderson, 1975a; Van Miller et al., 1975). Furthermore, only about one-tenth of the absorbed dose is excreted prior to metabolism to more polar compounds (Matthews and Anderson, 1975a; Van Miller et al., 1975; Balin et al., 1975). A number of the less chlorinated PCBs (i.e., mono-, di-, tri-, and tetrachlorobiphenyls) are readily metabolized and excreted by birds and mammals. There is little evidence that fish can metabolize any PCB.

It has been adequately demonstrated that a number of mammalian species and the pigeon can readily degrade and excrete monochlorobiphenyls, primarily 4-chlorobiphenyl (Matthews and Anderson, 1975a; Block and Cornish, 1959; Hutzinger et al., 1972; Safe et al., 1975a,b,c). However, the rate of metabolism drops sharply as the number of chlorines per molecule increases. For example, the rate of metabolism and excretion of several PCB isomers has been shown to decrease as the number of chlorines increases in the following order: 4-chlorobiphenyl 4,4'-dichlorobiphenyl 4,4'-dichlorobiphenyl 2,5,2',5'-tetrachlorobiphenyl 2,4,5, 2',5'-pentachlorobiphenyl (Matthews and Anderson, 1975a; Van Miller et al., 1975; Matthews and Anderson, 1975b). The rate

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of metabolism and excretion of 4,4'-dichlorobiphenyl is approximately one-half that of 4-chlorobiphenyl. In each case the PCBs are metabolized primarily by hydroxylation and conjugation with glucluronic acid (Matthews and Anderson, 1975a; Balin et al., 1975). The importance of the route of excretion, i.e., urine or feces, is determined primarily by the degree of chlorination. Approximately 60, 30, and 7 percent of a single dose of a mono-, a di-, and a pentachlorobiphenyl, respectively, were excreted in the urine of rats. The remainder of the dose was excreted in the feces (Matthews and Anderson, 1975a).

Once the number of chlorine atoms on the biphenyl molecule reaches four, the position of the chlorine atoms becomes a more important factor in determining the rate of metabolism and excretion (Matthews and Anderson, 1975a; De Freitas and Norstrom, 1974). As was observed with the chlorinated benzenes (Jondorf et al., 1955; Jondorf et al., 1958) those PCBs which have two adjacent unsubstituted carbon atoms are metabolized and excreted more rapidly than PCBs having the same degree of chlorination, but which do not have two adjacent unsubstituted carbon atoms (Matthews and Anderson, 1975a). It is also likely that, as with the chlorinated benzenes, the absence of two adjacent unsubstituted carbon atoms has a greater effect as the degree of chlorination increases. For example, the initial half-life of 3,5,5',5'-tetrachlorobiphenyl is only about two-fold greater

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in the rat (Matthews and Tuey, 1976) than that of 2,5,2',5'-tetrachlorobiphenyl in the same species (Van Miller et al., 1975). On the other hand, the initial half-life of 2,4,5,2',4',5'-hexachlorobiphenyl appears to be infinite, whereas the initial half-life of 2,4,5,2',5'-pentachlorobiphenyl is only about two days (Matthews and Anderson, 1975a). This particular hexachlorobiphenyl has been shown to be in the highest concentration of any PCB found in the adipose tissue of the Swedish population (Jensen et al., 1974).

The importance of two adjacent unsubstituted carbon atoms to the metabolism of PCBs may be derived from their effect on the formation of arene oxide intermediates during the metabolism of these compounds by the hepatic mixed-function oxidases. Evidence for the formation of arene oxide intermediates in PCB metabolism was first provided by Gardner et al., (Gardner et al., 1973) in their study of the metabolism of 2,5,2',5'-tetrachlorobiphenyl and in a later study of 4-chlorobiphenyl metabolism by Safe et al., (1975c) which was specifically designed to provide evidence of an arene oxide intermediate. Metabolism of PCBs which do not have two adjacent unsubstituted carbon atoms by hepatic mixed-function oxidases, via direct hydroxylation of the biphenyl molecule and/or the formation of an arene oxide between a chlorinated and an unsubstituted carbon atom could occur, but each of these mechanisms would be expected to be slower than arene oxide formation between two unsubstituted carbon atoms (Daly et al., 1972; Jerina and Daly, 1974). The latter mechanism would be expected

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to result in dechlorination and/or shifting of a chlorine atom (Daly et al., 1972). The metabolism of selected hexachlorobiphenyls has been reported (Jensen and Sundstrom, 1974; Hutzinger et al., 1974; Hass, unpublished), and in two incidents (Hutzinger et al., 1974; McKinney et al., unpublished) dechlorination and/or chlorine shifting was observed, but in all cases the rate of metabolism was quite slow.

Thus, those PCBs which are more readily metabolized and excreted may also more readily form arene oxides. Certain arene oxides have been implicated as potential carcinogens (Daly et al., 1972; Jerine and Daly, 1974) as have certain PCB formulations (Ito et al., 1973; Kimbrough and Linder, 1973; Kimbrough et al., 1975), but there is no published evidence which indicates that the less chlorinated PCB formulations have been so rigorously tested.

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ANIMAL TOXICOLOGY

Introduction

A number of reviews on different aspects of the toxicology of the PCBs have been written recently and no effort has been made in this report to give a complete outline of the animal toxicology (Kimbrough, 1974; Peakall and Risebrough, 1975; Nelson et al., 1972; Fishbein, 1974).

The material summarized in this report consists predominantly of more recently published information on toxic effects of PCBs in mammals and experimental studies in birds. Since Nelson et al. (1972) discussed the toxic effects produced in fish by PCBs extensively, the reader is referred to this and the other reviews cited above for information on toxicity of PCBs in this species.

The emphasis of the present review was placed on chronic toxic effects wherever possible. Unfortunately, very little information was available for halogenated dibenzofurans and the brominated biphenyl mixtures.

Acute Toxicity

Polychlorinated Biphenyls (PCB)

The acute oral LD_{50} of the PCBs in rats, rabbits and mice ranges from 1 to 10 g/kg body weight (Tables 5,6). There is some indication that young animals may be more sensitive than adults,

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and females more sensitive than males (Table 5). According to the classification used by the American Industrial Hygiene Association (Hodge & Sterner, 1949), the acute toxicity of the PCBs can be classed as slightly toxic (0.5 to 5 g/kg body weight) to practically non-toxic (5-15 g/kg body weight).

The symptoms assocatiated with administration of a toxic dose of PCB (Aroclor 1242) in rats consist of diarrhea, diminished exploratory behavior, decreased response to pain stimuli, chromodacryarrhea, adipsia, oliguria, anorexia, erythema of limbs, followed by ataxia, coma and death. Death occurred up to 14 days following administration of the toxic dose. 24 hours after administration of a single toxic dose of Aroclor 1242, gross pathology indicated all organs appeared normal except the liver and kidneys. No inflammation was observed in the abdominal and intestinal mucosa. Histopathological findings showed large discrete sudanophilic vacuoles in the hepatocytes. Widely scattered foci of tubular epithelial cells were present in the kidneys (Bruckner, et al., 1973). However, Kimbrough (1974) reported ulceration of the gastric and duodenal mucosa in rats after single oral doses of 3,000 mg/kg Aroclor 1254 or 1260.

Only one metabolite of PCB is known to have been tested for the acute LD_{50}. The 5-OH metabolite of 2,4,3'4'-tetrachlorobiphenyl was known to be more toxic than the parent compound (0.43 g/kgBW/2.15 g/kgBW (Table 5). Dermal toxicity of PCB is summarized in Table 7.

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Polybrominated Biphenyls (PBBs)

Polybrominated biphenyls show a low order of acute toxicity to the rat (Table 8). In the case of chicks, a 37% mortality was reported when PBB was administered in the diet at a level of 400 ppm, for 15 days. Seven out of eight guinea pigs fed 50 ppm dietary PBB died (Vos and VanGerderen, 1973). Effects noted included cortical atrophy of the thymus, adrenal enlargement, marked depletion of the follicles and periarteriolar lymphocytes sheath of the spleen.

Chlorinated Dibenzofurans

See subacute toxicity.

Chlorinated Napthalenes

See end of chapter.

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TABLE 5

Compound Tested	Species	Route	g/kg body wt. LD_{50}	Reference
Aroclor 1254	Rat(Adult-Sherman Strain)	oral	4-10	Linder, et al. (1974)
" 1260	Rat(Adult-Sherman Strain)	oral	4-10	"
" 1254	Rat(weanling " ")	oral	1.295	"
" 1260	Rat(weanling " ")	oral	1.315	"
" 1254	Rat(female " ")	Intravenous	0.358	"
" 1221	Rat(female " ")	oral	4.00	Panel on Hazardous Trace Substances (1972)
" 1262	Rat(female " ")	oral	11.3	
" 1240	Rat	oral	4.25	Bruckner, et al. (1973)
" 1254	Rat(Wistar-30-day-old M-F)	oral	1.3	Grant & Phillips (1974)
" 1254	Rat(Wistar-60-day-old M-F)	oral	1.4	"
" 1254	Rat(Wistar-120-day-old M)	oral	2.0	"
" 1254	Rat(Wistar-120-day-old F)	oral	2.5	"
Kaneclor-400	Rat(Wistar Strain - Male)	oral	1.30 (ml/Kg)	Ikeda, et al. (1970)
Kaneclor-400	Rat(Wistar Strain - Female)	oral	1.14 (ml/Kg)	
Kaneclor-400	Mice(CFI Strain - Male)	oral	1.875 (ml/Kg)	
Kaneclor-400	Mice(CFI Strain - Female)	oral	1.57 (ml/Kg	
Kaneclor-300	Rat(Wistar Strain - Male)	oral	1.15	
Kaneclor-300	Rat(Wistar Strain - Female)	oral	1.05	
BP-200 (biphenyls of dicloride and below	Mice(dd-strain-female)	oral	6.36	Kitamura (1972)
2,4'-dichlorobiphenyl	Mice(dd-strain-female)	oral	7.86	"
trichlorobiphenyl	Mice(dd-strain-female)	oral	3.06 - 4.25	
biphenyl of trichloride and below	Mice(dd-strain-female)	oral	9.27	"
2,4,3',4'-tetrachlorobiphenyl	Mice(CFI strain)	Intraperitoneal	2.15	Yamamoto & Yoshimura (1973)
5-OH derivative of 2,4,3'4'-tetrachlorobiphenyl	Mice(CFI strain)	"	0.43	"
2,3,4,3'4'-pentachlorobiphenyl	Mice(CFI strain)	"	0.65	"

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TABLE 6

Oral LD_{50} (Rat) (Panel on Hazardous Substances, 1972)

Compound Tested		g/Kg body wt.
Aroclor 1221	(undiluted)	3.98
Aroclor 1232	(undiluted)	4.47
Aroclor 1242	(undiluted)	8.65
Aroclor 1248	(undiluted)	11.0
Aroclor 1260	(50% soln in corn oil)	10.0
Aroclor 1262	(50% soln in corn oil)	11.3
Aroclor 1268	(50% soln in corn oil)	10.9

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TABLE 7

Skin MLD_{50} Rabbits (Panel on Hazardous Substances, 1972)

Compound tested		g/Kg body wt.	
Aroclor 1221	(undiluted)	>2.000	<3.169
Aroclor 1232	(undiluted)	>1.26	<2.0
Aroclor 1242	(undiluted)	> .794	<1.269
Aroclor 1248	(undiluted)	> .794	<1.269
Aroclor 1260	(50% soln in corn oil)	>1.26	<2.0
Aroclor 1262	(50% soln in corn oil)	>1.26	<3.16
Aroclor 1268	(33.3% soln in corn oil)	>2.5	

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TABLE 8

LD_{50} Polybrominated Biphenyls

Compound	Species	Route	LD_{50}	Reference
Firemaster BP6	Rat	Oral	21.5 g/Kg	Hill Top Research, Inc. (1970) for Michigan Chemical Company
Octabromobiphenyl	Rat	Oral	More than 2 g/Kg	Aftosmis, et al., 1972
Octabromobiphenyl	Bobwhite Quail	Oral	More than 12.5 g/Kg	"
Hexabromobiphenyl	Rabbit	Dermal	More than 5 g/Kg	"
Octabromobiphenyl	Rabbit	Dermal	More than 10 g/Kg	"

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SUB-ACUTE AND REPRODUCTIVE EFFECTS OF PCB'S, PBB'S AND CHLORINATED DIBENZOFURANS

A. Mammalian Sub-acute Effects of PCBs

In contrast to the acute toxicity (oral and dermal) of the PCBs which is of relatively low order when the substances are administered as a single dose, aspects of sub-acute toxicity of both the PCBs and individual chlorinated biphenyls appear to be of far greater concern exhibiting species sensitivity and cumulative toxic effects following continuous exposure at low levels.

When groups of mice were given toxic rice bran oil containing 1,600 ppm PCBs or 5000 ppm of PCB mixture with 48% chlorine, the toxicity response was similar in the two groups (Nishizumi 1970).

In a group of rats fed 2000 ppm of Phenochlor DP-6, deaths occurred between the 12th and 26th days with enlarged livers, atrophy of the spleens and a progressively induced hepatic porphyria was noted (Vos and Koeman, 1970). Administration of 1000 ppm of Arochlor 1254 in the diet of rats resulted in deaths between the 28th day and 53rd day (100% mortality) of feeding (Tucker and Crabtree 1970), 50% mortality at the same dosage in an 8-month study was reported by Kimbrough et al. (1972).

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Two groups of 52 male Sherman strain weanling rats were fed 100 ppm Aroclor 1242 (6.6-3.89 mg Aroclor/kg body weight) and 100 ppm Aroclor 1016 (6.9-3.5 mg Aroclor/kg body weight) respectively for 6 months and 54 rats were fed ground chow. Groups of 4 rats were sacrificed at intervals. Microscopic examination of the liver showed evidence of lipid accumulation, enlarged liver cells, inclusions in a number of livers and hemorrhage and necrosis in one animal per experimental group each. No difference in effect between the two compounds was noted (Burse et al., 1974).

Rats given 100 mg Aroclor 1242/kg body weight by stomach tube every other day for 3 weeks showed histopathological changes only in the liver and kidneys as foci of sudanophilic vacuolation but no overt sign of toxicity (Bruckner et al., 1973).

Rats (Sprague-Dawley) given 100 ppm of 2,5,2', 5'-tetrachlorobiphenyl in the diet for 3 weeks showed less liver hypertrophy and fewer biochemical changes than rats given a similar dose of Aroclor 1248 (Allen et al., 1975).

Administration of 100 mg/kg body weight of Aroclors 1242, or 1254 orally to rabbits once a week for 14 weeks resulted in enlarged livers with apparent destruction of the rough endoplasmic reticulum and atrophy of the uteri, while Aroclor 1221 did not cause this effect (Koller and Zinkl, 1973).

MONS 052458

The unusual sensitivity of mink to PCBs was reported by Aulerich et al., (1973) who noted 100% mortality within 6 months following administration of 30 ppm PCB (10 ppm each of Aroclor 1242, 1248 and 1254) to adult mink. Feeding of Aroclor 1254 at levels of 5 and 10 ppm in the diet for 4 months led to a dose-dependent retardation of weight gain of growing female mink. Platonow and Karstad (1973) produced 100% mortality in mink when they fed this species 3.6 ppm Aroclor 1254 in the diet for 105 days.

Rhesus monkeys are also very sensitive to PCBs (McNulty, 1975). For example, adult female rhesus monkeys (Macaca Mulatta) have been fed diets containing 2.5, 5.0 and 25.0 ppm of Aroclor 1248 over periods ranging from 2 months for the higher PCB levels to 1 year for the two lower doses (Allen et al., 1974; Barsotti and Allen, 1975). Animals on the 25 ppm dose developed facial edema, alopecia and acne within 1 month, and 1 of 6 animals had expired as a result of PCB intoxication 2 months after removal from the diet. The total intake of PCBs ranged from 250 to 400 mg/animal. As was the case with the higher doses, these animals developed anemia, hypoproteinemia, bone marrow atrophy and severe hypertrophic hyperplastic gastritis. PCB concentrations in subcutaneous adipose tissue averaged 127 ppm at termination of experimental diet and 34 ppm 8 months later. Surviving animals continued to show clinical signs and lesions of PCB intoxication 2 years following PCB exposure (Allen, 1975).

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When adult rhesus monkeys were fed diets containing 2.5 and 5.0 ppm Aroclor 1248 for 1 year, the females of the group developed periorbital edema, alopecia, erythema and acne from lesions that involved the face and neck within 1 to 2 months (Allen et al., 1974; Allen, 1975). Although males consumed more PCB, they exhibited only moderate periorbital edema and erythema. An abnormal dysplastic growth pattern of the gastric mucosa was also noted in male rhesus monkeys fed 300 ppm Aroclor 1248 for 3 months (Allen and Norback, 1973).

Cygomegalous or squirrel monkeys fed different dietary levels of Kanechlor 400 showed weight loss, palpebral edema, enlargement of the liver and pneumonia. The lowest effective total dose was 300 mg/kg bw given over 20-32 weeks (Nishizumi, 1970).

A rhesus monkey fed 3 ppm Aroclor 1242 for 8 months died spontaneously and on autopsy was found to possess a gastric lesion manifested by extensive down growth of the epithelium deep into the subserosa and into the muscular wall of the stomach itself (McNulty, 1975).

One monkey fed 2,4,4'-trichlorobiphenyl and another fed 2,4,5,4'5'-pentachlorobiphenyl at 10 ppm for 90 days were reported clinically well and autopsies showed no positive findings (Oregon State University, 1975; McNulty, 1975).

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Third-litter sows received feed containing Aroclor 1242 at a concentration of 20 ppm throughout gestation and nursing. Treated sows differed significantly from control sows in the number of live pigs farrowed. Treated sows also had more mummified fetuses. Performance of live-born pigs was not affected by feeding PCB to the sows during nursing. Pathologic changes in the sows included hypertrophy of the liver and erosion of the stomach. Slight atrophy of the spleen and thyroid gland were observed in pigs from treated sows (Hansen et al., 1975).

Dermal toxicity studies in rabbits of technical PCB samples that contain an average of 60% chlorine (Phenoclor DP6, Clophen A60, and Aroclor 1260) as well as fractions containing tetra and pentachlorodibenzofuran have been recently described by Vos and Beems (1971). PCB-induced skin lesions were hyperplasia and hyperkeratosis of the epidermal and follicular epithelium following application of 118 mg of the three PCBs (5 times per week for 38 days) in the back skin of adult female New Zealand rabbits. Histopathology of the liver included centrolobular degeneration, centrolobular liver cell atrophy, focal necrosis, and cytoplasmic hyalin degeneration. PCB-induced kidney lesions were hydropic degeneration of the convoluted tubules and tubular dilation with the presence of casts. Definitive hyperplasia and hyperkeratosis of the follicular epithelium of the ear skin were seen after the topical application of fractions of Phenoclor and Clophen, while the fraction from Aroclor caused a minimal hyperplasia and hyper-

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keratosis of the follicular epithelium. Other effects elicited by the dermal application of the PCBs including thymus atrophy and lymphopenia as well as elevated excretion of fecal coproporphyria and protoporphyria.

From the response of the back skin and the liver of the rabbit to the three PCB mixtures, and from the response of the ear to the 25% diethyl ether-hexane fractions it was concluded that there were definite quantitative differences in toxicity, at least between the samples used in the above study and prior studies. The extent to which these samples are representative of the normal commercial output has not been established and emphasizes the difficulty in the evaluation of toxicity data of PCBs in which the samples may differ in the amount and nature of toxic impurities.

Vos & Notenboom-Ram (1972) compared the toxicity of Aroclor 1260 with a single isomer 2,4,5,2',4',5'-hexachlorobiphenyl in New Zealand rabbits. Dermal applications of a total 120 mg Aroclor 1260 (5 times/week for 28 days) resulted in early macroscopic skin lesions. The lesions in a 2,4,5,2',4',5'-hexachlorobiphenyl group of rabbits treated similarly appeared later and were less severe.

When groups of 5 male mice were fed dietary levels of 10, 30, 100 and 300 ppm of the PCB isomers 3,4,5,3',4',5'-hexachlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl and 2,4,6,2',4',6'-hexachlorobiphenyl

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for 4 weeks it was noted that the 3,4,5,3',4',5', isomer of hexachlorobiphenyl caused death in mice at a dietary intake of 10 ppm (2.1 mg/kg bw) within 36-47 days of exposure while consumption of the other two isomers resulted only in death at a dietary level of 300 ppm (64.3 mg/kg bw). Body weight was reduced at the lowest dose for the 3,4,5,3',4',5', isomer and only at the highest dose for the other two isomers. Atrophy of the thymus and hepatomegaly was noted at the lowest dose in the mice receiving the 3,4,5,3',4',5', isomer and only this isomer produced experimental porphyria.

B. Avian subacute toxic effect of PCBs.

Chickens fed 10 ppm Aroclor 1242, or 100 ppm Aroclor 1254 showed diminished growth but a dietary level of 100 ppm Aroclor 1260 did not produce this effect (Keplinger, et al., 1971).

Symptoms of PCB poisoning in birds consist of tremor, ataxia, ruffling, loss of feathers. Edema of the subcutaneous tissues, and fluid accumulation of the abdominal and thoraxic cavities are characteristic signs at autopsy. These findings are responsible for this disease being designated chick edema disease. Several outbreaks of chick edema disease caused by PCBs have been reported (Firestone 1973, Kohanowa 1969a, 1969b).

Chicks (one day old white leghorn cockerels) were fed the following PCB isomers: 2,3,6,2',3',6'- hexachlorobiphenyl 2,4,6,2',4',6' hexachlorobiphenyl, 2,3,4,2'3',4'-hexachlorobiphenyl,

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2,3,6,2',3',6', hexachlorobiphenyl and 2,4,5,2',4',5' hexachlorobiphenyl for 21 days at a level of 400 ppm. The isomer 2,4,5,2',4',5' hexachlorobiphenyl was also fed at the dietary level of 100 ppm. The 3,4,5,3',4',5' isomer was the most toxic causing death of all chicks within 11 days after onset of exposure. These chicks had chick edema disease, atrophy of the thymus and loss of subcutaneous and visceral adipose tissue. The other isomers also caused weight loss the 2,4,6,2',4',6' isomer being the least effective. Liver enlargement was noted for all groups the 2,3,6,2',3',6' being the least effective and the 2,4,6,2',4',6' the most effective. The microscopic findings made in the liver were most pronounced in the group fed the 2,4,6,2', 4',6' isomer. (Since the chicks fed the 3,4,5,3',4',5' isomer died relatively early in the experiment pathological findings in the livers of these chicks are not comparable to those made for the other isomers.)

When chicks were fed 5% rice oil which had produced Yusho they developed chick edema in 17 days. Similar symptoms were produced when chicks were fed 400 ppm Kaneclor 400 (Goto et al., 1969).

C. Mammalian Reproductive Effects of PCBs

Oral administration of 0.025 mg/day of Clophen A60 in peanut oil to NMRI-mice for 10 weeks lengthened the estrus cycle from 6.6 $\pm$ 2.5 days to 8.7 $\pm$ 4.3 days (Orberg and Kihlstrom, 1973; Kihlstrom et al., 1973). Females treated analogously for 62 days

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and mated with untreated males exhibited a significant decrease in the implantation rate from 87.0% in the controls to 79.5%. Male castrated mice were given 0.25 gm PCB (Clophen A 60) in peanut oil/day by stomach tube for 28 days and 70 μg testosterone propionate daily on days 19-28. The dry weight of the seminal vescicles after this treatment period was compared to castrated male mice given testosterone but not PCB and was found to be significanlty reduced.

Groups of 10 NMR I female mice were injected subcutaneously with 50 mg/kg body weight of Clophen A 60 in peanut oil or only the vehicle on the day of parturition and thereafter once weekly for 3 weeks. The 209 offspring were bred when reaching sexual maturity by mating them in pairs as follows: 17 pairs of controls, 19 pairs where the males had received Clophen A 60 as a suckling, 23 pairs where the female had received Clophen A 60 as sucklings and 23 pairs were both sexes had received Clophen A 60 as sucklings. The controls had an average of 11.5 offspring per litter while the parents where both mates received PCBs as sucklings had 8.8 offspring per litter. The resorption rate for both groups was the same but the number of implantations were reduced. Reproduction was not affected where only one mate received the PCB (Kihlstrom et al.,1975).

Keplinger et al.,(1972) reported low mating indices and decreased survival of pups for rats receiving Aroclor 1242 at 100 ppm, and decreased survival of pups receiving Aroclor 1254

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at 100 ppm. No reproductive effects were found with Aroclor 1260 at 1, 10, or 100 ppm, or with Aroclor 1242 or 1254 at 1 or 10 ppm. These studies suggest that in mammals reproductive effects decrease with increasing chlorination.

Sherman rats were exposed to polychlorinated biphenyls, Aroclor 1254 and Aroclor 1260. Rats exposed to Aroclor 1254 at dietary levels of 20 ppm or more had fewer pups per litter than the controls in the F1b and F2 generations (Linder et al., 1974). The 100 ppm exposure level of Aroclor 1254 increased mortality in the F1b offspring and markedly decreased mating performance of the F1b adults. The 500 ppm dietary level of Aroclor 1260 reduced litter size and decreased survival in the F1 litters. Dietary levels of 5 ppm Aroclor 1254 and 100 ppm Aroclor 1260 had no effect on reproduction in rats exposed through two generations. Liver weights were increased in 21-day-old F1 male weanlings at the 1 ppm level of Aroclor 1254 and in either sex of F1 and F2 weanlings at 5 ppm or higher levels of both Aroclor 1254 and 1260. Histological changes in the liver and increased liver weights were observed in adult rats exposed to the higher levels. Pregnant rats given Aroclor 1254 at the rate of 100 mg/kg/day on days 7-15 of gestation produced grossly normal litters, but only 30.1% of the pups survived to weaning. Reproduction and pup survival were not affected at dosage rates of 50 mg Aroclor 1254/kg bw/day or 100 mg Aroclor 1260/kg bw/day.

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Rabbits have been found to be more sensitive to PCBs than rats in regard to fetotoxic and reproductive effects (Villeneuve et al., 1971). In rabbits, no effects were reported at dosages of 6.25 or 10 mg Aroclor 1254 /kg/day, but at dosages of 12.5 to 50 mg/kg/day, fetotoxic effects were noted. Abortions, maternal death and stillborns occurred, but no consistent skeletal abnormalities were found.

Ringer et al., (1972) found that 1 ppm of Aroclor 1254 caused a slight reduction in reproductive success in mink, but at 5 ppm Aroclor 1254 complete reproductive failure was noted. In the same study 12 mink were fed a diet containing 30% Coho Salmon from Lake Michigan. None of the mink whelped while 11 of 12 controls whelped.

Female adult rhesus monkeys fed Aroclor 1248 at a level of 25 ppm for 2 months noted at beginning of the 5th month experienced either fetal resorption or abortion during their second month of pregnancy (evidenced by regression in uterine size and reestablishment of menstruation (Allen et al., 1974). A third animal carried her fetus to term. This infant's weight was considerably lower than the average rhesus infant (375g vs 544 $\pm$ 101g) and had 25 μg PCB/g/(ppm) of adrenal and adipose tissue. Adult female rhesus monkeys fed 2.5 and 5.0 ppm Aroclor 1248 were bred to control males following the establishment of a relatively steady tissue level of PCB at 6 months. Following 3 mating, 12.5% of the 5 ppm group and 37.5% of the 2.5 ppm group was pregnant

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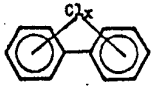
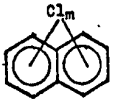
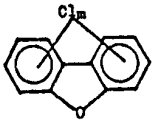
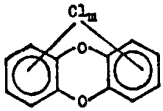
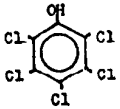
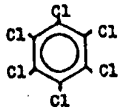
Appendix A
CHLORINATED AROMATIC COMPOUNDS
REFERRED TO IN CHEMISTRY REPORT

NAME	STRUCTURE	EXTENT OF CHLORINATION POSSIBLE	NUMBER OF CHLORINATED DERIVATIVES POSSIBLE
Chlorinated biphenyls		x= 1-10	209
Chlorinated naphthalenes		m=1-8	75
Chlorinated dibenzofurans		m=1-8	135
Chlorinated dibenzo-p-dioxins		m=1-8	75
pentachlorophenol		-	-
hexachlorobenzene		-	-

MAR 10 1978

FINAL REPORT OF THE SUBCOMMITTEE ON THE HEALTH EFFECTS OF POLYCHLORINATED BIPHENYLS AND POLYBROMINATED BIPHENYLS

JULY 1976

DEPARTMENT OF HEALTH, EDUCATION AND WELFARE

WASHINGTON, D.C.

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ERRATUM - Table numbers proceed from 9 to 11. There is no Table 10.

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SUBCOMMITTEE ON THE HEALTH EFFECTS
OF
POLYCHLORINATED BIPHENYLS
AND
POLYBROMINATED BIPHENYLS

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SUBCOMMITTEE ON THE HEALTH EFFECTS
OF
POLYCHLORINATED BIPHENYLS
AND
POLYBROMINATED BIPHENYLS

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2. Metabolism and Biochemical Toxicity

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A. Gardner
L. Garthoff
J. Goldstein
Y. Ku
H. Matthews, Chairperson
J. Moore

3. Animal Toxicity and Carcinogenesis

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L. Fishbein
G. Flamm
L. Kasza
R. Kimbrough, Chairperson
W. Marcus
S. Shibko
R. Teske

4. Human Exposure

F. Cordle, Chairperson
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B. Hackley
R. Lehman
J. McLaughlin
R. Rhoden
R. Shapiro

5. Staff Support

H. Gerstner
J. Moore
R. Shapiro

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Subcommittee on the Health Effects

of PCBs and PBBs

Purpose:

1. "Assemble, review and interpret data that assess the health significance of polychlorinated biphenyls."

2. "Formulate recommendations as to future research needs."

Specific Objectives:

1. Chemistry:

   Assess the impurities that may be found in PCBs and PBBs, the "hardness" of the data giving their potential for accumulating in the food chain.

2. Metabolism and Biochemical Toxicity:

   Assess the Metabolism of PCBs and PBBs and the possible contribution of specific isomeric homologs to the observed toxicity; evaluate possible effects at the cellular level; and define existing dose-response relationships for the phenomena.

3. Animal Toxicity and Carcinogenicity

   Assess the short and long term effects, including carcinogenis, of exposure to PCBs and PBBs in various animal models, their relationship to known human effects, and the establishment of dose-response curves.

x

4. Human Exposure

Quantity known human exposures, accidental pulsed, and long range, their relationship to possible overt symptomatology, and the establishment of possible dose-response curves.

MONS 052350

INTRODUCTION

PCBs were reportedly first synthesized in 1881 by Schmidt and Schultz, but were not available commercially until 1930[1] (Hubbard, 1964). From 1930 until 1970, when their distribution in the U.S. was voluntarily restricted by Monsanto to closed systems, the use of PCBs in a wide variety of industrial applications had steadily increased.

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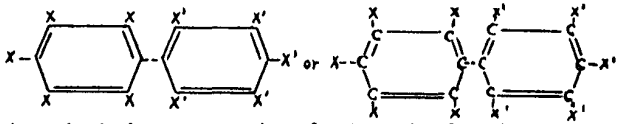
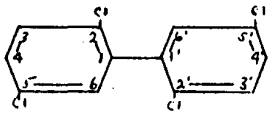
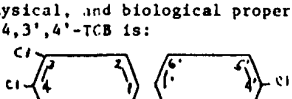
1. Commercial PCBs are complex mixtures. Arochlor 1254, for example, contains 69 different molecules (Zitko, 1971), which differ in the number and position of chlorine atoms.



This is a chemical representation of a PCB molecule. C = carbon atom, X = Cl (chlorine atom) or H (hydrogen atom). The basic parent molecule contains two benzene rings connected by a carbon-carbon bond. When all the X' and X are hydrogen, the molecule is called biphenyl. When several of the hydrogen atoms are replaced by chlorine atoms, the molecule is called a PCB. X and X' are used to indicate that the chlorine atoms are on different benzene rings. For example, the chemical structure for 2,5,2',5'-tetrachlorobiphenyl is:



Positional isomers have the same number of chlorine atoms, but they are located at different positions on the ring. 2,5,2',5'-tetrachlorobiphenyl and 3,4,5',4'-tetrachlorobiphenyl (TCB) are isomers. They are different molecules with different chemical, physical, and biological properties. The chemical structure for 3,4,3',4'-TCB is:



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The problem of polychlorinated biphenyls (PCBs) became of national concern in 1971, when several accidental contaminations of foods were reported. In addition, the extent of the environmental contamination, and its persistence, were not precisely known. Subsequently, various regulatory actions were taken by the concerned agencies involved and, with the cooperation of the only U.S. producer, the situation was felt to be under control.

Then, in 1975, the reported high levels of contamination, with PCBs, of Hudson River fish, refocused national attention on this environmental contaminant. It was soon apparent that the actions and control measures of the early 1970's had not succeeded in totally reducing, or even substantially alleviating the problems associated with this environmental pollutant.

On November 17-19, 1975, a National Conference on Polychlorinated Biphenyls, sponsored by the Environmental Protection Agency in cooperation with the Department of Agriculture, Council on Environmental Quality, Department of Health, Education and Welfare and Department of the Interior, was held in Chicago, Illinois. This conference brought together the latest data, and scientific expertise, to consider all aspects of the various problems associated with PCBs, and the means for their possible resolution.

In his introductory remarks to the Session on Health Effects and Human Exposure, Dr. David P. Rall, Session Chairman, announced the formation of a Subcommittee on PCBs of the DHEW Committee to

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Coordinate Toxicology and Related Programs. The Subcommittee was given the charge to:

1. Assemble, review and interpret data that assesses the health significance of polychlorinated biphenyls.

2. Formulate recommendations as to future needs.

The accidental contamination of animal feeds with polybrominated biphenyls (PBBs), and consequent human exposures, that occurred in the State of Michigan, has been approached not only on its own basis, but in comparative relationship to the PCBs, as well. Therefore, the scope of this Subcommittee was expanded to the Subcommittee on the Health Effects of PCBs and PBBs. Members of this Subcommittee came from within the Department of Health, Education and Welfare, as well as including consultants from other Federal Agencies concerned with this difficult problem.

The report which follows represents the culmination of this Subcommittee's efforts.

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GENERAL
SUMMARY AND CONCLUSIONS

CHEMISTRY

The great complexity of PCB commercial mixtures has provided the difficult task of separating the components of these mixtures and determining the complete identity of the compounds. Efforts to define these mixtures have been quite successful over the past several years (Hutzinger et al., 1974). Identification of the component chemicals in PCB residues presents another difficult problem. Little progress has been reported in this area. Since the fate of components of commercial PCB mixtures entering the environment cannot be followed directly, inferences must be drawn about chemical alteration of chlorinated biphenyl compounds in the environment mainly based on laboratory studies.

The known resistance of aryl chlorides to chemical oxidation and hydrolysis presumably was a major factor in the promotion of PCBs for industrial uses. Exposure to non-metabolic environmental agents is unlikely to result in significant oxidation or hydrolysis of chlorinated biphenyls. However, since appreciable photoalteration of chlorianted biphenyls has been observed using either sunlight or sunlight-simulating lamps in the laboratory (Hutzinger et al., 1974) as energy sources, it is highly probable that photochemical changes occur in the environment. These photochemical studies have indicated that reductive dechlorination to biphenyls

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of lower chlorine content is a predominant alteration route although formation of more polar compounds, including a chlorinated dibenzofuran, has also been reported (Hutzinger et al., 1974; Crosby and Moilanen, 1973). The diverse conditions of the environment make it difficult to predict accurately the end products and rates of photoalteration of chlorinated biphenyls. From a comparison of carbon-halogen bond-energies, brominated biphenyls might be expected to be more readily altered by light than chlorobiphenyls. But because of the lower volatility and different end uses of bromobiphenyls, they may not be as readily exposed to light as the chlorinated analogs.

A typical PCB residue from fish resembles the Aroclor 1254 mixture more closely than it does other Aroclors (Zitko et al., 1972; Veith, 1975). Considering the major components of Aroclor 1254 (Sissons and Welti, 1971) it appears that penta-, hexa-, and heptachlorinated biphenyls tend to concentrate at this trophic level in the biosphere. It is of considerable interest, therefore, to carry out comparative accumulation, metabolism and toxicity studies emphasizing these higher chlorinated biphenyls using compounds of known chlorine substitution pattern. Individual chlorinated biphenyls are now quite accessible through synthesis and recent studies have begun to obtain these types of biological data.

Studies using a group of five symmetrical hexachlorobiphenyl isomers in chicks (McKinney et al., in press) and in mice (Biocca,

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1975) indicated that distinct difference in toxicity are possible and these differences could be related to structure. The isomers with chlorine substituents in the 4,4' positions appeared to accumulate more rapidly in adipose tissue, showed increased activity in the liver and greater overall toxicity (McKinney, 1975; McKinney et al., in press). Comparison of two pentachlorbiphenyls in laying chicks again indicated the one isomer with 4,4'-substitution to have greater toxic effects (Ax and Hansen, 1975; Ax et al., 1976). Structure-activity relationships, particularly for biphenyls known to be major components of commercial PCB mixtures, could be useful in assessing the potential hazard of these compounds.

A major part of determining human exposure to PCB residues in foods is evaluating the adequacy of the analytical methodology used and the significance of the data obtained. The methods applicable to PCB determination are complex and to be judged adequate should give acceptably reproducible results in the hands of experienced analysts. The degree of success of inter-laboratory collaborative studies helps measure the adequacy of a method.

PCB residues are multicomponent mixtures. Many common chlorinated pesticides are extracted from samples along with the PCBs. Procedures for separation of PCB residues from interfering pesticides therfore bec ie important as a prerequisite to quantitation. Several different quantitation techniques have been used (Hutzinger et al., 1974). Comparison of PCB residue data is difficult where standardization of the quantitation procedure is lacking.

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It has been shown that recovery of PCB mixtures purposely added to food samples, using commonly applied analytical methodology, varies with the average level of chlorination. Recoveries tend to decrease with increasing chlorine level (Stalling et al., 1972).

Analytical procedures for determination of PCB and PBB (the latter is predominantly a hexabromobiphenyl) residues are essentially similar. They differ somewhat in cleanup of the extract and in the use of a higher column temperature for gas chromatographic determination of the PBB residue. The limit of quantitation for PCBs is generally 0.2 ppm for individual foods and about 0.05 ppm for Total Diet composites using Food and Drug Administration methodology. For PBB residues, the limit of quantitation is approximately 0.05 ppm in fats and 0.01 ppm in non-fatty foods. Interlaboratory studies of analytical methods for PBB determination have not been reported.

The chlorinated dibenzofurans (Cl-DBFs) have become a focus of concern as the class of contaminant compounds in commercial PCBs most likely to contribute significantly to the toxicity of the PCB mixture. This concern presumably stems mainly from the demonstrated toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin and the similarity in structure between dibenzo-p-dioxin and dibenzofuran (NIEHS Conference, 1973; also see Appendix of Chemistry Report) and from the little toxicity data that has been published for Cl-DBFs (Bauer et al., 1961). Recent data indicated

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the toxicity of 2,3,7,8-tetrachlorodibenzofuran approaches that of the analogous dibenzo-p-dioxin at least in chicks and in guinea pigs (Moore et al., 1976). If the chlorinated dibenzo-p-dioxins can serve as an example, chlorinated dibenzofuran toxicity can be expected to vary with number and position of chlorine atoms on the parent ring system. Relationships between structure and toxicity will emerge as more Cl-DBFs are synthesized and tested for toxicity.

A range of Cl-DBFs (from dichloro through hexachloro) have been reported in various Aroclors (Roach and Pomerantz, 1974b; Bowes et al., 1975a) and two specific compounds, the 2,3,7,8-tetrachloro- and 2,3,4,7,8-pentachloro-dibenzofurans, have been identified (Bowes et al., 1975b). Quantitation of Cl-DBF contaminants in PCB mixtures, a difficult procedure, suggests total Cl-DBF levels in the low parts per million range (Nagayama et al., 1975; Bowes et al., 1975a). The presence of Cl-DBF in a synthesized, individual, symmetrical chlorinated biphenyl has been reported (Moron et al., 1973). Chemical analysis of these individual chlorobiphenyls may be necessary prior to their use in toxicological and other biological studies.

There have been no published positive findings of Cl-DBFs in environmental samples or in foods other than rice oil. The finding of Cl-DBFs in such samples would not necessarily implicate commercial PCBs as the source of these contaminants since Cl-DBFs (generally the higher chlorine levels) have been reported in other

MONS 052358

industrial chemicals (Firestone et al., 1972; Schwetz et al., 1974; Villanueva et al., 1974). It is also possible that Cl-DBFs may be formed or altered in the environment.

METABOLISM AND BIOCHEMICAL TOXICITY

The effect of PCBs and PBB on the hepatic mixed-function oxidase (MFO) enzymes has been the most thoroughly studied of any biochemical parameter that they are known to alter. On a molar basis, the PBBs are approximately five-fold more potent than the PCBs in inducing increased levels of the MFO enzymes (Farber and Baker, 1974). Among the PCBs it appears as if their potency increases with increasing chlorination and chlorine substitution in the para > ortho > meta positions respectively (Echobichon, 1975). However, this induction of the MFO enzymes is not unique to these compounds and the induction observed is well within the range observed with many other xenobiotics. The PCBs are somewhat unique as MFO inducers in that they induce the formation of both Type I and Type II P-450 (Alvares et al., 1973), but this induction may have been due to the fact that the commercial formulation used in the study was a mixture of twenty or more PCBs which were metabolized to an even greater number of metabolites. In addition, many, if not most commercial PCB formulation contain trace amounts of chlorinated dibenzofurans (Araki, 1974). These compounds may be up to 170 times more potent as MFO inducers than the PCBs. The chlorinated dibenzofuran concentration of American

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PCB formulations is usually quite low when they are produced, however, the effect of long-term is unknown. In any case, since induction of the MFO enzymes may result in increased hormone metabolism or carcinogen activation, exposure to the PCBs and PBBs should be limited on that basis alone.

PCBs and PBBs administered at relatively high concentrations, usually 50 ppm or higher in the diet, to laboratory animals have been shown to cause prophyria (Goldstein et al., 1975), disfunction of the thyroid (Bastomsky, 1974), inhibition of various enzymes (Pardini, 1971), changes in the liver to body weight ratios (Garthoff et al., 1975) various disorders of the liver (Kimbrough et al., 1975), and to alter the level or utilization of corticosteroids (Wasserman et al., 1973) and vitamins A, D and E (Cecil et al., 1973; Wong et al., 1974; Combs et al., 1975). Certain of the less chlorinated PCBs have also been shown to have a mild estrogenic effect when tested in the immature rat and mouse (Kihlstrom, 1973; Nelson, 1974). However, most of these parameters have not been studied in sensitive species or demonstrated at low exposure levels in laboratory animals.

The available data imply that the PCBs and PBBs containing six or fewer halogen atoms are readily absorbed from the gut of higher animals. The available data also imply that the PCBs are not excreted to an appreciable extent prior to metabolism to more polar compounds, and that long term PCB storage is in the skin and adipose tissue (Matthews and Anderson, 1975a). Studies of PBB

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metabolism are not yet available. Since tissue samples from birds and mammals with known exposures to PCBs usually contain only those PCBs with five or more chlorine atoms, it is assumed that the less chlorinated PCBs have been metabolized and excreted. On the other hand there is little evidence that fish can metabolize any PCB and an analysis of fish tissue usually shows a PCB pattern very similar to that to which the fish were exposed (Stalling and Mayer, 1972).

Laboratory studies have demonstrated that the rate of PCB metabolism and thus excretion is approximately inversely proportional to the degree of PCB chlorination so long as there are two adjacent unsubstituted carbon atoms on the biphenyl molecule. When two adjacent unsubstituted carbon atoms are not present the biological half-life of the given PCB may be a matter of years and accumulation of high tissue concentrations with continued exposure is inevitable (Matthews and Anderson, 1975a). It should be noted that the major constituent of Firemaster BP-6 does not have two adjacent unsubstituted carbon atoms and that the corresponding PCB has been shown to have an extremely long half-life in the laboratory rat and probably the human population as well.

It should also be noted that metabolism can also result in further complications of the PCB problem because those PCBs which are most readily metabolized and excreted are those which are most likely to be metabolized via arene oxide intermediates. And where as the reactivity of arene oxides varies greatly and often

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ultimately determines the toxicity, mutagenicity or carcinogenicity of the parent compound (Jerina and Daly, 1974), the PCBs offer such a range of degree and position of substitution that it would not be unlikely to find that one or more of these PCB metabolites would have the proper stability to be a mutagen or a carcinogen. Thus a move from the more highly chlorinated PCB formulations to the less chlorinated ones may help solve the long-term residue problem only to intensify other problems.

ANIMAL TOXICOLOGY

Gleaning the information that is now available on animal toxicology makes it obvious that different commercial mixtures of PCBs elecit different toxic responses in animals, and that different animal species vary in their susceptibility to the toxic effects of PCBs. Reproduction is severely affected in mink at a dietary level of 5 ppm Aroclor 1254, and a slight effect is still noted at a dietary level of 1 ppm (Ringer et al., 1972). In rhesus monkeys reproduction was reduced at a dietary level of 2.5 ppm of Aroclor 1248 (Allen 1975). In rats a dietary level of 20 ppm Aroclor 1254 depressed reproduction while in the same rat strain (Sherman), in a study conducted simultaneously in the same laboratory, a dietary level of 500 ppm Aroclor 1260 was necessary to reduce reproduction (Linder et al., 1974). In comparative studies done with European products, Phenoclor DB6 and Clophen A60, and the American product, Aroclor 1260, the

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European products were more toxic to chickens than the American product (Vos & Koeman, 1970). The difference in toxicity in this study was attributed to contamination of the European products with chlorinated dibenzofurans and perhaps chlorinated naphthalenes. However, if the differences in the effect on reproduction by the different Aroclors are compared, the contamination with chlorinated dibenzofurans may not be the decisive factor.

Hepatic porphyria has been produced in a number of species, namely the chicken, rabbit, Japanese quail and rat, by a number of commercial mixtures, such as Clophen A60, Phenoclor DP6, Aroclor 1016, 1242, 1254, and 1260 (Vos and Koeman, 1970, Vos and Beems, 1971, Iverson et al., 1975, Goldstein et al., 1974, 1975). It (hepatic porphyria) has not been reported in the monkey, mink or human (see Yusho) mammalian species quite susceptible to the toxic effects of PCBs in other ways. Aroclor 1254 and Aroclor 1242 produced hepatic porphyria in the female rat at doses lower than Aroclor 1016. Again, different commercial mixtures produce this toxic effect at different dosage levels. The hepatic porphyria occurs concomitantly with an increase in ALA synthetase in the liver. Mixed function oxidases are also induced in the liver and comparative studies with PCB isomers have suggested that if the 4,4' positions on the biphenyl ring are occupied by chlorine atoms the effect is most pronounced (Ecobichon and Comeau, 1975).

The liver is the primary target organ for PCBs in the rat. Early changes include hepatomegaly with a concomitant increase

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in smooth endoplasmic reticulum, lipid accumulation at higher dietary levels (20 ppm for Aroclor 1254 and 1260) and ultrastructural changes such as atypical mitochondria and the formation of concentrically arranged membranes surrounding lipid vacuoles and fingerprint inclusions in the hepatocytoplasm. Increasingly noted with either higher levels or longer exposure (Kimbrough, 1974).

These changes are not as pronounced with Aroclor 1242 or 1016. Similar changes have been reported in the primate (Allen, 1975).

In the mouse, liver tumors have been produced with Aroclor 1254 (Kimbrough and Linder, 1974) and Kanechlor 500 (Ito et al., 1973) and in the rat with Kanechlor 400 (Kimura and Baba, 1973) and Aroclor 1260. Some tumors have also been produced with Aroclor 1242, 1254 and 1260 (Kimbrough, 1976). In rats in a separate study in one study with Aroclor 1260, some of the tumors were classified as hepatocellular carcinomas (Kimbrough et al., 1975). The dietary levels of the PCBs in these studies were 100 ppm or more, a high level when compared to the daily average human intake of PCBs but not very high for subgroups with a high intake of fish from polluted waterways or in some occupational situations. This is emphasized by the fact that the dietary levels which produce tumors and the relatively low dietary levels which affect reproduction (2.5 ppm in the monkey and 0.5 ppm in the mink) of some commercial PCB mixtures do not represent a no effect level. It is presently not known what the no effect levels are. Other uncertainties

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contribute to these problems. The Yusho oil which caused a poisoning outbreak in Japan was not only contaminated with PCBs but also with high levels of chlorinated dibenzofurans.

In the primate, in addition to the effect on the liver, the gastric mucosa (Allen and Borback, 1973), the skin, and the Meibomian glands are also affected at comparatively low dietary levels and the bone marrow is depressed (Allen 1975) while the gastric mucosa of the rat is only affected at exceedingly high doses (Kimbrough, 1974). Whether the dog also shows an affect on the gastric mucosa needs clarification. In the rabbit, atrophy of the thymus is a toxic manifestation in addition to liver pathology (Vos and Beems, 1971). Fluid accumulation occurs in primates, chickens, and finches. The lymphatic system is also affected in minks.

The few studies conducted with some hexachlorobiphenyl isomers demonstrated that the 3,4,5,3',4',5' hexachlorobiphenyl was the most toxic while 2,3,6,2',3',6' hexachlorobiphenyl was the least toxic isomer (Biocca et al., 1975). Penta-, hexa- and heptachlorobiphenyls are preferentially retained in mammalian adipose tissue for extremely long periods of time (Kimbrough, 1975) (at fairly high concentrations in the rat for a recovery period of 16 months). Whether this has an influence on the toxicity of PCB mixtures has not been determined.

The toxic effects of the contaminants of PCBs have not been extensively studied. While it is assumed that chlorinated

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naphthalenes are toxic within the same dosage range as the chorinated biphenyls, the chlorinated dibenzofurans probably have a greater toxicity. It is assumed that 2,3,7,8 tetrachlorodibenzofuran is the most toxic of this group of compounds. This compound also shows marked species variation. While the single oral LD_{50} in guinea pigs is between 5 and 10 ug/kg bodyweight, 1000 ug/kg TCDF given orally had no effect on rats. Mice are equally insensitive to the toxic effects of TCDF (Moore et al., 1976).

For the brominated biphenyls limited toxicity data are only available on mixtures containing predominately hexa- and octabromobiphenyl. Both mixtures differ sufficiently in isomeric composition so that their toxic effects may quantitatively be quite different and also different from the PCBs. Again the problem of toxic contaminants has not been resolved. If toxic effects are similar to PCBs then, at least in some species such as mink and monkey, longterm low level exposure should result in measureable toxicity. Additional animal studies are needed to resolve some of these problems. Poor metabolism and excretion of the brominated biphenyls may lead to long retention of these compounds predominantly in adipose tissue with accumulation to very high levels on continued exposure. Whether this would lead to sufficient recirculation of the chemicals to cause toxic effects on target organs in presently not known.

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HUMAN EXPOSURE

Several reports (Jelinek & Corneliussen, 1975; Humphrey, 1976; Kutz and Yang, 1975; Dennis, 1975; Kleinhert, 1975; Hesse, 1975; Yobs, 1972; Kutz and Strassmman, 1975) provide evidence that would indicate that a substantial proportion of the population of the United States has been exposed to PCB's. Minimal human exposure of the population to PCB's has occurred from food, air and water, while significant human exposure appears to be limited to sports fishermen consuming fresh water fish from contaminated streams and lakes, and to occupational exposure in industrial workers.

Jelinek & Corneliussen (1975), in reviewing data from the FDA Total Diet Study (1971-1975) report that all food classes of the total diet have declined to no PCB occurrences except in these meat-fish-poultry composites. About 40 percent of these composites continue to contain detectable residues of PCB's, although only traces have been detected in the latter years. The fact that levels in these composites have declined to only traces further support the inference that the meat, poultry and eggs no longer contain detectable PCB's and that the low level findings are probably due to the fish in these composites. This would imply that the PCB levels in the diet may have "bottomed out" and may remain static until such time as there is a change in the PCB residues in fish.

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Data compiled from studies sponsored by the National Marine Fisheries Service (NMFS) also support the continuing presence of PCB residues in fish. A compilation of PCB data, representing the results of all the measurements known to NMFS on PCB's in fish used in the U.S. diet, indicates several important points: (1) while at one time or another, some PCB measurements have been made on many fish, there is an inadequacy of information on PCB residues in the most important fish items in the fish diet; (2) sampling and analysis have been sporadic and not designed to measure trends in human exposure; and (3) systematic surveys of neither the important items nor the species most likely to be contaminated have been undertaken.

However, these survey data do show that in general U.S. fish eaters include a wide variety of fish items in their diet and that some 93 percent of the U.S. population (197 million) consume fish, with the average annual consumption of fish being 15 pounds/year/fish eater.

At present, it is difficult to estimate all human exposure to PCB from eating fish, either from the population as a whole or subgroups at higher risk of consuming large quantities of fish with higher PCB residues. Fragmentary evidence from NMFS data suggests that the exposure of the population as a whole from PCB residues in ingested fish is probably well below 19 mcg/day/consumer, based on PCB levels which are estimated to be below 1 ppm and 19 g of fish consumed/day. This can be compared to

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the results of the FDA Total Diet Study where it has been estimated that the overall PCB daily intake is on the order of 5-10 mcg/day for the general population. The lower FDA estimate is based on the methodology of the Market Basket Survey where fish are purchased at the consumer level and would not be applicable to diets which include a high consumption of fish from certain areas with high PCB residues.

A recently completed study (Humphrey et al., 1976) has attempted to assess some of the consequences of human exposure to PCBs from the high consumption of fish from contaminated areas. The results of this study show that a group of sports fishermen consumed an average of 24-25 pounds of fish/person/year, with the highest individual exposure for a two year period reported as 180 pounds per year. PCB residues in cooked fish ranged from 0.36 to 5.38 ppm. Although there was a wide range of blood PCB levels for each quantity of fish consumed, there was a highly significant correlation between the reported quantity of Lake Michigan fish consumed and the concentration of PCB in the blood of study participants, with the higher reported fisn consumption being associated with higher PCB blood levels. The blood values ranged from a low of 0.007 ppm in the control group (fish consumption less than 6 pounds/year) to a high of 0.366 ppm in the exposed group (fish consumption 24-25 pounds/year).

These investigators calculated that the amount of PCB ingested by the exposed group could average 46.5 mg/year and ranged from

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compared to 90% in the control group (Allen, 1975). The conception rate of females bred to PCB-fed males was equally as great as that in females bred to control males.

D. Mammalian Sub-Acute and Reproductive Effects of PBBs

Male Sprague Dawley rats maintained on diets containing 0, 0.1, 0.01 or 1% octobromobiphenyl for 30 days did not exhibit overt toxicity during this period. Gross pathological studies revealed enlarged livers and some kidney changes (petechial hemorrhage, enlargement), while histopathological changes in the 1% group included liver lesions consisting of centrilobular cytoplasmic enlargement and vaculation and kidney lesions consisting of hyaline degenerative cytoplasmic changes (Aftosmis et al., 1972). Thyroid hyperplasia was observed in all rats in all test groups.

Rats were fed 100 and 1000 ppm octabromobiphenyl in their diets and then a number were sacrificed after 2 and 4 weeks of feeding and after 2,6 and 18 weeks of recovery on an octabromobiphenyl-free diet. The hepatocytes were markedly enlarged in rats fed 100 ppm and 1000 ppm of the PBB after 2 weeks of treatment. Histopathologic changes were characterized by hepatocellular hypertrophy with the pathologic changes localized mostly in the centralobular zone (Aftomis et al., 1972b). The cytoplasmic inclusions were more pronounced in the livers of rats fed 1000 ppm than 100 ppm of the PBB. There was some evidence of recovery since the livers of the 100 ppm level animals returned almost to normal 2 weeks after

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withdrawal of the compound.

Preliminary 28-day feeding studies in rats with octabromobiphenyl at 100 and 1000 ppm demonstrated liver enlargement, hepatocellular alterations with cytoplasmic inclusions and accumulative effects of bromine in the fat, liver and muscle (Aftosmis et al., 1972).

Norris et al., (1974) demonstrated hematological changes, liver enlargement and liver and kidney lesions at all levels of octabromobiphenyl (10, 000, 1000 and 100 ppm) in the diet of rats. When three groups of primagravid rats fed diets containing 100, 1000 or 10,000 ppm of octabromobiphenyl (BB-8) from day 6 through 15 of pregnancy and the pups delivered on day 20, anasarca was observed in one fetus at each of the two highest levels and gastroschisis was observed in another fetus at each of these levels. No other gross effects were observed in either the mothers or the pups and dose-related levels of bromine were found in the fetuses (Aftomis et al., 1972a).

When 1 g/kg of octobromobiphenyl was applied in corn oil under occuluded conditions to rabbits for 5 hrs/day for 10 days over a 2-week period, liver enlargement was found while at 0.1g/kg no enlargment was found (Aftosmis, et al., 1972b).

Hexabromobiphenyl (Firemaster BP-6) fed to pregnant Sprague-Dawley rats and Swiss/ICR mice (100 and 1000 ppm) resulted in a dose dependent decrease in mean fetal weight. (Number of pregnant

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mice: 16 controls, 9 received 100 ppm and 12 received 1000 ppm. Number of pregnant rats: 12 controls, 7 received 100 ppm and 6 received 1000 ppm). Exencephaly was produced in the offspring of the mice that received both 100 (3/121)and 1,000 ppm (2/174 dosages while cleft palate (4/87) and defective kidneys (2/87) were noted in offspring at the 1,000 ppm level. Nonpregnant mice fed 1,000 ppm PBBs for 11 days showed marked increase in liver size and weight (Corbett et al., 1975).

Cows from the Halbert herd received feed containing PBB at a level of 2914 ppm at a consumption rate of approximately 15 lbs/head/day (200 cows) or 8 lbs/head/day (200 cows) for a period of approximately 16 days. Early signs of toxicity included anorexia, decreased milk production, increased frequency of urination, lacrimation, some lameness, and shrinking of the udder of recently freshened cows. Upon removal of the contaminated feed appetite improved. Cows bred 4-6 weeks prior to onset came back in heat suggesting early resorptions.

Later signs exhibited by the cows included hematomas, abscesses, weight loss particularly in high producing cows, abnormal hoof growth, rough hair coat, alopecia, thickening of skin, dystocia, lack of udder development at freshening, metritis, and negligible milk production in cows freshening 3-4 months post-exposure. Cows also exhibited a lack of wound healing, general weakness and were highly susceptible to stress. Six months post-exposure non-lactating cows showed depression of

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appetite, prepartum weakness, failed to develop signs of labor and died without calving. Gross pathology included liver and renal degeneration, and hematomas and abscesses in the peritoneal and thoracic cavities.

Twelve 6 to 18 month-old heifers and bulls were offered the contaminated feed ad libitum. Five of the animals were dead within 6 weeks. Younger animals became prostrate, went through a short period of coma and died. Signs and lesions included testicular atrophy, abdominal adhesions, and massive liver abscesses. At 5 months only 2 animals remained alive. These became anorexic, would consume only milk and developed signs of hyperkeratosis over the entire body (Jackson and Halbert, 1974; Welborn, 1975).

The health status of 16 herds of dairy cattle exposed to low levels of polybrominated biphenyl (PBB) was compared with that of 15 control herds. Milk production of the contaminated herds was not significangly changed in 1972, 1973, and 1974, and was not significantly different from that of control herds in the same years. Mortality of adult cows and calves, the percentages of cows culled from the herds because of old age and low production, disease, or sterility, and the general health conditions were similar in the two groups. Serum concentrations of calcium, glucose, and cholesterol in contaminated herds were significantly different from those of the control herds, but the relationship to PBB exposure needs further investigation (Mercer et al., 1976, In Press).

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A study consisting of an investigation of records and herd history of herds accidentally exposed to PBBs was also done. Significant findings included a decrease in production of 20 to 50%; severe weight loss at calving time; sterility; decreased growth rate in young animals; evidence of soreness and stiffness; poor response to therapy of common diseases; prolonged wound healing; abnormal hoof growth; calf losses; and malformed calves. (Deming, 1975).

Polybrominated biphenyl was administered to four cows at a dose rate of 10 mg/head/day for 60 days. Although the study was not designed as a toxicology study, retrospective evaluation of the data provided no evidence of clinical problems among test animals during the period of exposure to PBB nor for a year thereafter (Fries and Marrow, 1975).

E. Chlorinated Dibenzofurans - Mammalian Toxicity

It is presently assumed because of our experience with the chlorinated dibenzodioxins, that the 2,3,7,8-tetrachlorodibenzofuran is the most toxic compound of this group of chemicals, while the dibenzofuran itself or the octadibenzofuran have little inherent toxicity on an acute basis (Kimbrough, 1974).

Baucr et al., in 1961 demonstrated the toxicity of mixtures of tri and tetrachlorodibenzofurans. A single dose of 1 mg or 0.5 mg/kg body weight given orally to rabbits caused severe and often fatal liver necrosis. Application of this material to the rabbit

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ear caused severe hyperkeratosis at the application site.

The single oral LD_{50} for tetrachlorodibenzofuran for guinea pigs is between 5 and 10 μg/kg. Symptoms of toxicity were severe weight loss, atrophy of the thymus and spleen. Hemorrhages were observed in the adrenals, urinary bladder and single cell necrosis was noted in the liver. C. D. Strain rats given as much as 1000 μg/kg bw of the TCDF failed to show any symptoms of toxicity and microscopic examination of their tissues did not reveal any abnormalities. Similarly oral single doses of up to 6000 μg/kg body weight of TCDF failed to elicit any toxic effect in C57Bl mice. A subcutaneous dose of 6000 μg/kg bw given to these mice produced weight loss, hepatomegaly and atrophy of the thumus but no fatalities (Moore et al., 1976).

While these findings indicate that in mice TCDF is 30 fold less toxic than TCDD, the overall estimated difference in toxicity between TCDD and TCDF is about tenfold (Bauer et al., 1961; Kimbrough, 1974; J. G. Vos, personal communication).

F. Chlorinated Dibenzofurans - Avian Toxicity

When 1 day old chicks were started on daily oral doses of 5 μg/kg TCDF daily most of them died within 11.5 days. One of 6 chicks died given daily oral doses of 1 μg/kg bw. Symptoms of toxicity at the low as well as the high doses consisted primarily of weight loss, decreased food consumption and general unthriftyness. At autopsy the most striking findings were subcutaneous edema, ascites and hydropericardium and atrophy of the thymus.

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An inflammatory exudate was noticed on microscopic examination in the lung and the pericardial surface of the heart showed inflammatory changes. Congestion and hemorrhage into the gastrointestinal tract was also observed (Moore et al., 1976).

G. Brominated Dibenzofurans - Mammalian Toxicity

When daily doses of 4 µg/rabbit of 2,3,7,8-tetrabromodibenzofurans were applied to the rabbit ear for 5 days giving a total dose of 20 µg/rabbit or about 5-6 µg/kg bw, the rabbits (4) developed hyperkeratosis of the treated ear and areas of liver cell necrosis (Kimbrough, personal communication). No other information is presently available on the toxicity of brominated dibenzofurans.

H. Longterm Toxicity Including Tumorogenesis

Chlorinated biphenyls

Mice

When male BALB c/J mice were fed Aroclor 1254 for 11 months at a dietary level of 0 or 300 ppm (49.8 mg/kg body weight) 22 of 50 mice in the experimental group and 24 of 50 in the control group survived. The livers of the test animals were markedly increased in size, and showed a qualitative increase in porphyrin. A total of 9 experimental mice showed 10 neoplastic nodules (hematomas, hyperplastic nodules) in their liver ranging in size from 0.1 - 0.5 cm in diameter. Other morphological changes observed in the livers of the experimental group including pleomorphism,

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areas of necrosis, and foci of adenofibrosis. (Kimbrough and Linder, 1974). Neither tumors nor the other morphological changes were noted in the controls. Only one of 24 surviving male BALB c/J mice fed Aroclor 1254 for 6 months followed by a control diet for 5 months had a hepatoma (neoplastic nodule) measuring 0.3 cm in diameter.

Ito et al., (1973) fed male dd mice 500, 250, 100 and 0 ppm Kanechlor 500, 400 and 300 in the diet respectively. After one year, hepatocellular carcinomas were observed in 5/12 mice fed Kanechlor 500 at a dietary level of 500 ppm, the other 7 mice in this group had nodular hyperplasia (neoplastic nodules?). No metastases were observed. Feeding α, B, or Y hexachlorocyclohexane (BHC) isomers with or without Kanechlor 500 at a dietary level of 250 ppm to mice for 24 weeks did not produce any tumors in the liver of animals receiving only the PCB (Ito et al., 1973). Liver tumors were observed in mice receiving 250 ppm α BHC alone or 250 ppm PCB and either 100 or 50 ppm α BHC or 250 or 100 ppm B BHC. Thus PCBs enhanced the tumor development of liver tumors of α or B BHC isomers.

Rats

Dietary exposure of male Sherman strain rats to levels of 500 ppm Aroclor 1254 (36.4 mg/kg body weight) for 6 months resulted in pronounced lipid accumulation in the liver which persisted for a 10 months observation period following the discontinuation of

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the dietary exposure to PCBs. Adenofibrosis (cholangiofibrosis) which was observed in the livers of rats ingesting the PCB for 6 months was still present 10 months later. Whether this lesion is persistent could not definitely be determined since high levels of the higher chlorinated biphenyl isomers were still present in adipose tissue and liver (Kimbrough, et al., 1973). Adenofibrosis is a focal proliferation of glandular epithelium forming ducts often surrounded by extensive fibrosis. This lesion usually occurs concomitantly in rat livers with hepatocellular carcinomas and has been produced by many known hepatocarcinogens. It was first described by Edwards and White (1941). The extremely long retention of some PCB isomers in rats was again noted when male Sherman strain rats were fed 100 ppm Aroclor 1254 for 6 months and then allowed to recover for 16 months. 4.4 ppm of PCB derived material was present in the liver and 152 ppm in adipose tissue on a wet weight basis (Kimbrough, 1976).

Continued dietary exposure to commercial PCB mixtures in mammals results in their storage in adipose tissue and over an extended period high levels may be attained (Curley, et al., 1971; Burse, et al., 1974). Blood levels are more a function of the dose, the rate of metabolism, availability of binding sites in blood, chemical characteristics of the compound given, rather than the amount stored in adipose tissue (Smrek, et al., in preparation).

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In another study, 200 experimental female Sherman strain rats were fed 100 mg/kg Aroclor 1260 in the diet (11.6 - 4.3 mg/kg body weight) for approximately 21 months and 200 female rats were kept as controls. A total of 184 experimental rats and 173 controls survived to sacrifice at 23 months. Hepatocellular carcinomas were observed in 26/184 experimental rats and in 1/173 controls. None of the controls but 146/184 experimental rats had neoplastic nodules within the liver (hyperplastic nodules). Areas of hepatocellular alteration were noted in 28/173 controls and 182/184 experimental rats. The incidence of tumors in other organs was not altered by PCB ingestion and metatases from the liver tumors were not observed (Kimbrough et al., 1975). Adenofibrosis of the liver was also noted in this study. In reporting these liver tumors the classification developed in a rat liver tumor workshop was followed (Squire and LeVitt, 1975).

Liver tumors (multiple adenomatous nodules) were also induced in 6/10 female Donryu rats with Kanechlor 400 but not in male rats. The dietary exposure varied throughout the study from 38-616 ppm (Kimura and Baba, 1973). The induction of liver tumors by known carcinogens in Sprague Dawley rats such as 3'methyl-4-dimethylamino-azobenzene, N-2-fluorenyl acetamide and diethylnitrosamine was inhibited by Kanechlor 500 (Makiura et al.,1974).

Groups of 50 male and female Charles River rats were fed dietary levels of 0, 1, 10 and 100 ppm of Aroclor 1242, 1254, and 1260 respectively (Calandra, 1976). At 3, 6, and 12 months after

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onset of the experiment, 5 rats per each group and sex were sacrificed. The surviving rats were sacrificied 24 months after onset of the experiment. The only body weight depression noted was observed in the female rats fed Aroclor 1254. The author reported that important histopathologic changes were only noted in the rats fed the different Aroclors for 24 months.

The liver weights were increased in the male and female rats fed 100 ppm of Aroclor 1260 and 1254 and only in females fed Aroclor 1242 at a dietary level of 100 ppm. It was noted that of a total of 20 surviving male and female rats (10 male and 10 female rats) fed 100 ppm Aroclor 1242 in the diet for 24 months 8/20 rats showed liver lesions called nodular hyperplasia, 2/20 had hepatomas and 1/20 had a cholangiohepatoma.

A total of 27 male and female rats (13 male and 14 female rats) survived to 24 months in the groups of rats fed 100 ppm Aroclor 1254 of these 13/27 had nodular hyperplasia of the liver 4/27 showed hepatomas and 2/27 showed cholangiohepatomas.

Similar findings were made in the total 27 surviving male and female rats fed 100 ppm Aroclor 1260 for 24 months. In these groups 7/27 male and female rats had nodular hyperplasia of the liver. 5/27 had hepatomas, and 2/27 had cholangiohepatomas.

Groups of 4 male and 4 female dogs were fed dietary levels of 0, 1, 10, and 100 ppm Aroclor 1242, 1254, and 1260 respectively for 2 years, 1 female fed 100 ppm Aroclor 1242, 1 male fed 10 ppm Aroclor 1242, 1 female dog fed 100 ppm Aroclor 1254, 1 female

fed 10 ppm and 1 male and 1 female fed 100 ppm Aroclor 1260 died. At the dietary level of 100 ppm of either Aroclor 1254 or Aroclor 1260 the body weight gain was slightly decreased for both sexes. Aroclor 1260 also reduced the body weight gain in the females at the dietary level of 10 ppm. In the beagles fed Aroclor 1260 at a dietary level of 100 ppm, the liver weight was increased and the serum alkaline phosphatase was elevated. All but 1 dog that died had either chronic peritionitis or chronic pneumonitis. Many of the dogs fed 10 or 100 ppm of different PCBs showed chronic inflammation of a variety of organs. Male dogs fed Aroclor 1254 showed diffuse hyperplasia of the interstitial cells of the testes and aspermatogenesis (Monsanto, 1971).

Decachlorobiphenyl

No long term studies are available.

Polybrominated Biphenyls

No long term studies are available.

Chlorinated Dibenzofurans and Chlorinated Naphthalenes

No long term studies are available.

Immunosuppressive Effects of PCB and PBB

Polychlorinated biphenyls (PCB) have been implicated as immunosuppressants. Friend and Trainer (1970) found a decreased resistance to duck hepatitis virus in PCB exposed ducklings.

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PCB has been shown to produce lymphoid atrophy in rabbits (Street and Sharma, 1975; Vos and Beems, 1971), chickens (Flick et al., 1975; Vos and Koeman, 1970) and guinea pigs (Vos and DeRoij, 1972; Vos and van Genderen, 1973). In addition, PCBs were found to suppress humoral immune responses to several antigens in rabbits (Koller and Thigpen, 1973, Street and Sharma, 1975) and guinea pigs (Vos and DeRoij, 1972, Vos and van Genderen, 1973) and to suppress cell mediated immune reactions in guinea pigs (Vos and van Genderen, 1973). In all of these studies the PCBs studied have been commercial mixtures; the role of contaminants such as chlorinated dibenzofurans needs to be considered.

The effect of HBB on the immune system was studied in chickens and guinea pigs (Vos and van Genderen). In chickens the atrophy of the lymphoid tissue was observed in bursal follicles and in the spleen. It suppressed the humeral immune response in guinea pigs.

MUTAGENICITY AND TERATOLOGY

Polychlorinated Biphenyls

The mutagenicity and cytotoxicity of PCBs, Aroclor 1242 and 1254, were studied by Green et al., 1975, a, b. The lack of mutagenic activity as measured by the dominant lethal test was reported for male Osborne-Mendel rats subjected to four different dosage regiment: (1) single oral intubations of 625, 1250 or 2500 mg/kg (for Aroclor 1242); (2) five daily doses of 125 or 250 mg/kg (for Aroclor 1242), 75, 150 or 300 mg/kg (for Aroclor

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1254); (3) five daily doses of Aroclor 1254 at 150 mg/kg, then starved overnight prior to mating; (4) chronic feeding for 70 days at a dietary level of 25 or 100 ppm prior to mating (Green et al., 1975a). In a second study, bone marrow and spermatogonial cells were cytogenetically investigated from Aroclor-treated Osborne-Mendel rats. Aroclor 1242 was given orally at single doses of 1250, 2500, or 5000 mg/kg or as four daily doses of 500 mg/kg/day; Aroclor 1254 was administered orally as five daily doses of 75, 150, or 300 mg/kg/day. No statistically significant increases in chromosomal aberations were found for the Aroclor-treated rats. As indicated by Green et al, (1975 b), while these studies were negative in regard to chromosomal mutations, they do not entirely rule out the possibility that PCBs may induce point mutations. To date, there are no known reports in the literature concerning the induction of point mutations by PCBs in laboratory model systems. The observations of Nilsson and Ravel, 1974, in Drosophila where no chromosomal breakage was found among Clophen A30- or A50-treated flies, are fully consistent with those of Green et al., (1975, a, b).

TERATOLOGY

Female NMRI mice, orally administered 0.025 mg/day of Clophen 60, showed evidence of an increased estrus cycle from 6.6 $\pm$ 2.5 days to 8.7 $\pm$ 4.3 days and a decreased ova implantation rate from 87.0 to 79.5% (Orberg and Kihlström, 1973). Kihlström et al., (1974 a), also demonstrated a decrease in the frequency of implanted ova

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among young animals nursed on milk containing PCB (Clophen 60). Both the male and the female contributed to the magnitude of the reduction of implantations. The mechanism by which exposure of the developing male to milk containing PCB leads to a reduction in the precent of ova implanted is unknown but need not necessarily involve dominant lethal events.

No reports of frank terata were found, but a number of studies indicated the facility of PCBs for placental transport. Grant et al., (1971 b), showed that the concentration of PCB in fetal tissue from oral administration of Aroclor 1254 was dose-dependent and that accumulation occurred in fetal liver where higher concentrations were found than in maternal liver. Placental transport of PCB has been reported for the rabbit, rat, mouse, and cow (Grant et al., 1971; Platonow and Chen, 1972; Berlin et al., 1975; Melvas and Brandt, 1973; Brandt and Ullberg, 1973). Evidence of placental transfer was also observed among Yusho patients. While PCB has no known or clearly defined teratogenic effect in mammals, their easy passage across the placenta suggests the possibility of potential for some form of fetal toxicity.

Chlorinated Dibenzofurans

No information available.

Brominated Biphenyls

15 pregnant rats were force fed 100 mg hexabromobiphenyl/kg

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body weight on days 6, 8, 10, 12, 14 and 16 of pregnancy in corn oil. 14 control rats were given corn oil. The pups were obtained by cesarian on day 19 of pregnancy. No terata were observed and no difference between control and experimental rats was noted in any of the other parameters studied.

5 control and 6 PBB treated animals were treated with colchicine and bone marrow was studied cytogenetically. Animals treated with PBB and colchicine had higher metaphase and mitotic indices than non-treated animals. Chromosome aberrations were not noted (Fiscor and Werts, 1976).

Toxicity of Chlorinated Naphthalenes

The following information is derived from a review published by the EPA, namely Environmental Hazard Assessment Report 'Chlorinated Naphthalenes', EPA-560/8-75-001*. For literature references please refer to this report.

Animal Studies

The following tables summarize the available studies in laboratory animals. Three routes of exposure are reported.

*This document is available through the National Technical Information Service, Springfield, VA 22151. 'Preliminary Environmental Hazard Assessment of Chlorinated Naphthalenes, Silicones, Fluorocarbons, Benzenepolycarboxylates and Chlorophenols'. (NTIS accession number PB-238-074/AS)

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TABLE 9

(a) Dietary Exposure

Compound	Species	Dose Level	Days Exposed	Effect Reported
Mono-			None reported	
Di-	Rat	5g/Kg feed	15	Increase in liver weight, growth impaired, rough coat.
Tri-	Mouse	2.5 mg/day	20	None.
Tri-	Rat	300 mg/day	9-136	Fatty infiltration of liver.
Tri/Tetra	Rabbit	15 mg/Kg body wt.	60	None.
Penta	Rat	50 mg day	63	Jaundice/fatty degeneration of liver.
Penta/Hexa-	Rat	300 mg/day	33	Death with yellow livers and extreme fatty degeneration.
Penta/Hexa	Rat	100 mg/day	55	Death with yellow livers and extreme fatty degeneration.
Penta-	Guinea pig	2.5 mg/Kg in oil	48	Death-Severe weight loss fatty degeneration of liver.
Hexa-	Rat	20 mg/Kg	84	Weight loss.
Hexa-	Rat	63 mg/Kg	84	Weight loss.
Hexa-	Rat	200 mg/Kg	84	Death.
Heptachloro-			None reported	
Octa-	Rabbit	1 g	Single dose	Death in seven days.
Octa	Rat	0.5, 2 or 5g/Kg	22	Decrease in liver but not plasma Vit. A.

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TABLE 10

(b) Inhalation Studies

Compound	Species	Dose Level	Days Exposed	Effect Reported
Tri-	Rat	0.05-0.2 mg/L	2 hr/day for 20 days	No toxic effect.
Tri-	Rat	1.31 mg/L	16hr/day for 134 days	No toxic effect.
Tri-	Rat	10.98 mg/L	16hr/day for 102 days	Slight liver discoloration, 5% rats showed increased fatty degeneration
Penta-	Rat	1.16 mg/L	16hr/day for 52 days	Jaundice, enlarged liver and 69% fatality.

No studies have been reported for the other chlorinated naphthalenes.

(c) Dermal Studies

Compound	Species	Conc Applied	Days of Application	Effect
Mono-	Rabbit(ear)	90 mg/g Acetone	5-7	Mild reddening.
Mono-	Rabbit(ear)	500 mg/g Acetone	5-7	Severe reddening, no decrease of sebaceous glands.
Tri-	Rat(skin)	Not given	2 hr/day/40-60 days	None reported
Tri-	Mice (skin)	Not given	2 hr/day/40-60 days	None reported
Penta-	Swine (skin)	60 mg/Lx3L	6 days/week-4 weeks	Slight hyperkeratosis.
Penta-	Rabbit(ear)	30 mg/g acetone/day	5	Mild dermatitis, hair folicular attenuation.
Hexa-	Rabbit(ear)	30 mg/g acetone	5	Decrease in sebaceous glands

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TOXICITY IN BIRDS

Turkey Poults

Penta/Hexachloronaphthalenes in the diet.

(a) 5 ppm for 40 days caused 23% reduction in weight gain with 6.5% mortality.

(b) 100 ppm - all poults died within 33 days. Histopathologic examination showed enlarged and darkened livers.

The LC_{50} was 20 ppm with an average decrease in weight of 51%.

Chickens

Penta/Hexachloronapthalene in the diet.

(a) No effects reported at dietary levels of 4 and 20 ppm (35 days).

(b) 100 ppm prevented egg production (35 days).

(c) 2550 ppm caused 100% mortality (14 days).

Effects reported included enlarged fibrous livers, lack of feather pigmentation and pericardial and peritoneal edema. A fourfold increase in Vitamin A in the diet decreased toxic effects.

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TOXICITY IN DOMESTIC ANIMALS

Ingestion is the most important route for exposure of domestic animals.

Cattle

Highly chlorinated naphthalene poisoning in cattle is known as bovine hyperkeratosis or X-disease. Detailed information on toxic doses is lacking. Penta/hexa mixture at a dose level of 5.5 mg/Kg body wt (orally) for 5 days caused a sharp drop in plasma Vit. A by the end of the third day and depressed plasma Vit. A for over 30 days. A single oral dose of 1 mg/Kg body wt of hexachloronaphthalene caused mortality within two weeks. The first effect of chloronaphthalene poisoning is an interference with the biotransformation of carotene to Vit. A. The Vit. A. deficiency is quickly followed by inflammation of the oral mucosa, lacrimation, excessive salivation and irregular food consumption. Gross physical effects that develop during the course of disease include a general thickening of the skin caused by over development of the skin's hairy layer with loss of hair (hyperkeratosis). There may be degeneration or irregular growth of the horns. Continued exposure results in anemia, dehydration, loss of weight, fever and death. There may be severe liver damage.

Swine

No toxic effects were observed at levels of 100 mg/Kg

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body wt of the chlorinated naphthalenes (degree of chlorination was not stated). 150 mg/kg body wt caused a marked depression of plasma Vit. A, and death occurred at a dose level of 198 mg/ Kg body wt.

Sheep

Toxic effects are observed at doses of chlorinated napthalene 10 X that required to produce toxicity in cattle. Sheep do not show cutaneous hyperkeratosis or an excessive drop in plasma Vit. A as observed in cattle.

Effects reported include nasal discharge, weakness, loss of weight, loss of appetite, ascites, necrosis and cirrohsis of the liver and cardiovascular effects.

Toxicity in Man

The most important route for mans occupational exposure to chlorinated naphthalene is via the inhalation route. Dermal absorption route may also occur.

Penta/hexachloronaphthalene at a concentration of 30 mg/g acetone, applied to the backs of human volunteers for a period of six weeks caused typical chloracne.

Daily topical application of mono-dichlorinated naphthalene to the human ear in mineral oil suspension for 30 days caused no observable effect. Two clinically distinct but oftern concurrent syndromes have been described, namely, liver necrosis, and chloracne

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with itching. A number of deaths involving acute atrophy of the liver have been reported; with the course of the disease similar to other forms of severe liver damage. Autopsy of fatally exposed workers show severe yellow atrophy of the liver. Definite data relating to dose response effects are in general lacking. However, two dermal studies with man have been reported.

SUMMARY

The degree of toxicity of chlorinated napthalenes increases with the degree of chlorination. The higher chlorinated naphthalenes (especially hexa and penta) have been associated with chloracne and liver damage in man. Dose response effects have not been established.

Cattle are more susceptible to the effects of chlorinated naphthalene than other domestic animals. The effects observed include development of Vit. A deficiency, hyperkeratosis and liver damage.

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HUMAN EXPOSURE TO POLYCHLORINATED BIPHENYLS

I. Introduction

Although the polychlorinated biphenyls (PCBs) have been used in a wide variety of industrial applications in the U.S. from 1930 until 1970, when their distribution was voluntarily restricted to closed systems, there is scant information on human exposure to adverse human health effects in the U.S. In the U.S., minimal human exposure of the population to PCBs is limited to food, air and water, while significant human exposure appears to be limited to sports fishermen consuming fresh water fish from contaminated streams and lakes; and to occupational exposure in industrial workers.

II. Dietary Exposure to PCBs

The May 1972 Report of the Interdepartmental Task Force on PCBs summarized the findings in food sampling programs conducted by the Food and Drug Administration and the Department of Agriculture. Jelinek et al., (1975) have provided an update to that summary and evaluated trends which is presented below.

The 1972 Task Force report outlined three broad sources of food contamination. These are restated here in order to show which sources have been effectively controlled and which sources apparently persist, as reflected by results obtained in continued food sampling.

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1. Environmental contamination - background levels of PCBs in fish from lakes and streams.

2. Industrial accidents - isolated incidents involving direct leakage and spillage or contact of PCB fluids and other PCB containing materials on animal feeds, feed ingredients or food.

3. Food packaging materials - PCB migration to foods packaged in PCB contaminated paper products.

As discussed in the 1972 Task Force report, there were a number of other positive findings in foods which could not be traced to one of these broad sources prior to 1972 and the source of such occasional findings remain speculative. However, in more recent years, essentially all positive findings of PCBs in the food supply have been attributable to one or more of these three sources.

Jelinek and Corneliussen (1975) reported that for the 1969-1975 period, there has been a significant decrease in PCB levels in all foods with the exception of fish, where no particular trend has been noted. From that observation they concluded that procedures instituted to exclude the use of PCBs in "open" applications have been effective, but that more needs to be done to prevent their entry into the acquatic environment.

Jelinek and Corneliussen (1975) presented data on FDA's sampling program showing a very conclusive decline in the FYs 1973-1975

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period in terms of occurrence rate of PCBs and maximum levels found in milk, eggs, cheese, animal feeds and components, processed fruits, and baby foods. Except for fish, occurrence rates in FY'75 had dropped to zero or less than 1% for all categories, and there were no findings in excess of the existing temporary tolerances. Similar data were presented covering USDA's sampling of meat and poultry which also showed a decline, to 0.3% positive and only 0.6% above the temporary tolerance.

Jelinek and Corneliussen (1975) also reviewed FDA Total Diet Study findings (FY'71-75) which showed that all food classes of the total diet have declined to no PCB occurrence and no calculable daily intake of PCBs, except in the meat-fish-poultry composites. About 40% of these composites continue to contain detectable PCBs, although only traces have been detected in the latter years. The limit of quantitative detection in the Total Diet Study is about 0.05 ppm; positive findings below that level are generally reported as traces since they are not reliably quantitated.

Occurrence of PCBs ended in 1973 in all other categories, notably in dairy product composites and the composites of grain and cereal products. This probably reflects the control measures effected on animal feeds and on the control of ingredients in recycled paper used for food packaging. What remains, based on the total diet study, is a continued low level occurrence (about 40% positive and only at trace levels) in the meat-fish-poultry

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composites. The fact that levels in these composites have declined to only traces further supports the inference that the meat and poultry and eggs no longer contain detectable PCBs and that the low level findings are primarily due to the fish in those composites. This would imply that the PCB levels in the diet may have "bottomed out" and may remain static until such time as there is a change in the levels for fish.

Estimates of dietary intake of PCBs based on the Total Diet Study must be taken as gross estimates because only traces are currently found and some type of estimated value must be assigned to those traces to calculate microgram per day intakes of PCBs. Jelinck and Corneliussen used a set of consistent assumptions for those traces in computing the daily intakes for the FY-1971-75 period. Their calculations showed a steady decline from 15 mcg per day down to 8.7 mcg/day, with all of this coming from the meat-fish-poultry group in FY'74-75 (minor and declining portions attributable to other food classes in earlier years.)

Review of this information implies that, although the various assumptions for trace residue reportings and varying food consumption data have a significant effect on daily intake calculations, an overall estimate in the order of 5-10 mcg/day PCB dietary intake of PCBs for th general public seems reasonable. This figure would not be applicable to diets which may include regular consumption of fish from certain locations with high PCB levels.

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III. PCB Residues in Fish

Review of the data gathered by various agencies on fish residues indicates a serious incompatability of sampling programs for obtaining data which reliably define trends in PCB levels. The Food and Drug Administration's primary concern is the levels which exist in the edible portion of commercially imported fish which are marketed interstate. Therefore, in most cases, the heads, entrails, skin and fins are excluded. Furthermore, FDA sampling has not included fish which are caught and consumed locally (freshwater fish) and the sampling has dealt with the most important consumption species which are primarily of marine origin and which generally do not contain PCB levels as high as freshwater species from certain locations.

In order to determine the human exposure to PCBs through dietary fish, one must know the levels of PCBs residues in the edible portions of fish, and the amounts of the various kinds of fish consumed by the population at large, and by special subpopulations. During the past few weeks, information has been compiled by National Marine Fisheries Service-NOAA on the PCBs levels of these residues in marine and freshwater fish and shellfish, and on dietary habits.

Table 11 lists the 20 most important types of fish eaten in the U.S. today, and the mean daily amount of each type eaten by

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TABLE 11

Fish and Shellfish Consumption in the United States
(September 1973-August 1974)

	Rank	Amount (mill.) lbs/yr)	Percent of total by wt.	Number of Actual Users (millions)	Mean amount per user (grams/day
Total		2957.	100.	197.	18.7
Tuna (mainly canned)	1	634	21.4	130.	6.1
Unclassified* (mainly breaded, incl. fish sticks)	2	542.	18.4	68.	10.0
Shrimp	3	301.	10.2	45.	8.3
Ocean Perch*	4	149.	5.0	19.	9.7
Flounder	5	144.	4.9	21.	8.6
Clams	6	113.	3.8	18.	7.6
Crabs/Lobsters	7	110.	3.7	13.	10.6
Salmon	8	101.	3.4	19.	6.7
Oysters/Scallops	9	88.	3.0	14.	7.8
Trout**	9	88.	3.0	9.	12.3
Cod*	11	78.	2.7	12.	8.1
Bass**	12	73.	2.5	7.6	12.0
Catfish**	12	73.	2.5	7.5	12.1
Haddock*	12	73.	2.5	11.	8.6
Pollock*	15	60.	2.0	11.	6.8
Herring/Smelt/ Sardines	16	54.	1.8	10.	6.7
Pike**	17	35.	1.2	2.5	17.4
Halibut*	18	32.	1.1	5.0	8.0
Snapper	18	32.	1.1	4.3	9.3
Whiting	20	25.	0.9	3.2	9.7
All other classified		152.	5.1	n.a.	n.a.

* Mainly imports
** Fresh water

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the subpopulations of actual users. The Table includes all dietary fish, from sport fishing and from domestic and imported commercial fishing. These 20 items comprise 95% of the fish products eaten. The results are taken from information in a recent Seafood Consumption Study by the National Purchase Diary of Schaumburg, Illinois, sponsored by the Tuna Research Foundation, and National Marine Fisheries Service data on the amount of fish and shellfish processed and distributed in the U.S. Several items in the Table are worth noting for purposes of the present analysis. (1) Although ninety-three percent of the U.S. population (197 million) eat fish, the average annual per capital consumption of fish is small: 15.0 lbs/year--fish eater; (2) a large "Unclassified" fish fraction exists in the U.S. diet, ranking just below tuna in importance; (3) the major portion of many of our most familiar types of seafood is imported; and (4) freshwater species, led by trout, bass, and catfish, comprise about 9% of our total fish diet.

A compilation of PCB Data, representing the results of all the measurements known to NMFS of PCBs in fish used in the U.S. diet is presented in the Compendium of PCB data. It includes data from government reports, and state and private publications. An effort was made to include current, unpublished data from marine laboratories. The compilation includes the results of a comprehensive literature search by the NOAA-Environmental Data Service (EDS). An EDS-ENDEX data search for unpublished data

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and a EDS-OASIS search were made, crossing marine food species with PCBs.

Two significant sources of data--the 1975 FDA-Market Basket results, and the results of the extensive Fall 1975 New York State Department of Environment analyses were not available to NMFS at the time Compendium was published. However, FDA has indicated that the 1975 Market Basket results do not differ dramatically from 1973/4 data. Preliminary results of the New York Study are included in Table 13.

Table 12 summarizes the PCB information assembled in the Compendium relating to the 20 most important kinds of dietary fish identified in Table11. Although at one time or another, some PCB measurements have been made on many fish, Table 11 points out the inadequacy of information on PCB residues in the most important items in the fish diet. Sampling and analysis have been sporadic and not designed to monitor trends in human exposure. Systematic surveys of neither the important items nor the species most likely to be contaminated have been undertaken. Very few recent (1975) measurements have been reported.

However fragmentary the data on PCB levels may be, they do not include a single measurement exceeding 1 ppm in any of the ten most important fish foods, except for Dover sole and crab taken in the immediate vicinity of Los Angeles sewerage outfalls, and crab living on contaminated sediments in Upper Chesapeake Bay.

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TABLE 12

Maximum Reported PCB Residue Levels in
Fish Muscle (White Meat)

Rank#	Kind	Range and Max. Level Reported (ppm) (see Compendium)	Mean Level in the U.S. Diet
1.	Tuna	0-0.49 (1973)	Unknown*
2.	Unclassified (mainly breaded)	no data	Unknown
3.	Shrimp	0-0.167 (1971)	Unknown*
4.	Ocean Perch	0-0.25 (1974)	Unknown*
5.	Flounder/Sole	0.6.3[a] (1972)	Unknown*
6.	Clams	0-0.819 (1974)	Unknown*
7.	Crabs/Lobster	0-4.9[b] (1972)	Unknown*
8.	Salmon	0-0.5 (1974)	Unknown*
9.	Oysters, Scallops	0-0.43 (1974)	Unknown*
10.	Trout (excl. Lake Trout)	0-0.56 (1972)	Unknown*
11.	Cod	0-0.4 (1974)	Unknown*
12.	Bass	0.3-8.4[c] (1974)	Unknown*
13.	Catfish	0-4.4[d] (1974)	Unknown*
14.	Haddock	0-1.16 (1974)	Unknown*
15.	Pollock	0.0 (1974)	Unknown*
16.	Herring/Smelt/ Sardines (marine	0-1.6 (1974)	Unknown*
17.	Pike	0-0.65 (1974)	Unknown*
18.	Halibut	0-0.149 (1974)	Unknown*
19.	Snapper	0-0.1 (1974)	Unknown*
20.	Whiting	0.0 (1974)	Unknown*

These 20 items compose 95% of the fish in the U.S. diet.

* Probably well below 1 ppm

[a]Single Dover Sole taken near Los Angeles municipal sewerage outfall. The mean value of Sole samples taken in this vicinity was 1.3 ppm in 1975. Mean values of other samples taken away from outfalls were less than 1 ppm in 1975. In any case, although Dover sole is an important food fish in Northern California, it is not taken commercially in Southern California waters.

[b]Single yellowneck crab taken near Los Angeles outfall-mean of group including this crab was less than 1 ppm. A composite of Upper Chesapeake Bay crab contained 1.2 ppm in 1974.

[c]Taken in 1974 from St. Croix River, Wisconsin--mean of 4 White Bass was 6.2 ppm.

[d]Taken from Mississippi River, Minnesota--mean of a sample of 5 catfish was 2.5 ppm.

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No more than 1.6 ppm has been reported in items 11 through 20 in importance, with the exception of freshwater bass and catfish living in river and lake areas known to be contaminated with PCBs. Nonetheless, as emphasized in the Table, there have been no PCB measurements on the important unclassified dietary fish items, and the analytical information is in no instance systematic enough to permit an estimate of the actual mean PCB values, hence human exposure. The strongest statement that can be made, based on the incomplete data summarized in the Compendium, is that most of the important fish meat items eaten in the U.S. probably contain mean PCB residue levels well below 1 ppm.

Fragmentary evidence also leads to the conclusion that the PCB levels in fish liver, roe and oil are approximately ten times that in the edible muscle and the PCB concentrations are greatest in the older larger oily fish, especially those that spend part or all of their lives in contaminated lakes, rivers or estuaries.

Table 13 lists the location of the species where high PCB levels, exceeding the FDA 5 ppm guideline, have been reported. Although the trout, salmon and chub in Lakes Michigan and Ontario and the Hudson River bass, perch and eel constitute only a few percent at most of the national fish diet, in some areas they are a significant part of the fish diets.

In order to discover what is presently known about U.S. fish consumption habits, a wide range of government and private sources

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TABLE 13

Areas Where at Least One Example of High* PCB Residue Levels Have Been Reported in the Listed Species

Species	Location
Striped Bass	Hudson River, New Jersey
Chub	Lake Michigan
Carp	Mississippi River, Minn., Lake Onandaga, NY
Chain Pickerel, Alewife	Hudson River
Coho Salmon	Lake Michigan, Lake Ontario, Hudson River
Chinook Salmon	Lake Michigan, Lake Ontario, Hudson River
Steelhead Trout	Lake Michigan, Lake Ontario
Lake Trout	Lake Michigan, Lake Ontario, Lake George, NY
Bass, Smallmouth	Lake Onandaga, Genessee River, NY Hudson River, Mohawk River, St. Lawrence River
White Perch	Lake Onandaga, Hudson River
Alewife	Hudson River
White Sucker	Hudson River, Mohawk River
Walleye	Hudson River, Mohawk River, Black River, NY
Bass, Largemouth	Hudson River, Mohawk River
Yellow Perch	Hudson River
American Eel, Crabs, Sturgeon	Hudson River
Rock Bass, Catfish	Hudson River
Bluefish	Long Island Sound (muscle from one large oily fish contained 8 ppm)

This Table includes recent data from New York State Department of Environmental Conservation not included in the NMFS Compilation.

The Hudson River above Fort Edward, New York, is not contaminated with PCBs and the residue levels in fish are quite low.

*Above the current 5 ppm FDA Guideline.

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were consulted. A number of pre-1970 studies are available, including a 1969 NMFS Survey of Fish Purchases and a 1968-70 HEW Ten State Nutrition Survey. In addition, a few specialized reports have been published, including annual FDA Regional Basket Surveys that do not include fish eaten in restaurants and institutions or by sport fishermen, and surveys by the Sport Fishing Institute and a 1974 Texas A&M Analysis of Seafood Consumption Patterns in Texas. However, the most up to date and comprehensive data are available in the previously mentioned 1973-74 Seafood Consumption Study by the National Purchase Diary.

Table 14 summarizes results of fish consumption demographic information that defines the number of U.S. consumers who would exceed an arbitrarily set dietary micro-constituent level. To date, this kind of information is available only for total dietary fish and one subcomponent, tuna. Table 14 indicates that 75 million U.S. consumers eat more than the national average of 18.7 grams of fish per day and 29 million would exceed the present dietary intake limit of PCB (175 mcg/day) if the 35 or more g/day of fish eaten was contaminated on average to 5 ppm, the current FDA guideline level. There is, of course, no evidence that the mean PCB level in fish is anywhere near 5 ppm. Nonetheless, should it in the future reach 1 ppm, then by an extrapolation from Table 14, an estimate can be made that about 200,000 U.S. consumers would be exceeding the 200 mcg/day FDA limit. As

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TABLE 14

Number of U.S. Consumers Who Eat More Than X

X (g/day)	Number (thousands of consumers) Total Fish	Tuna
0	197,000	130,000
18.7 (national avg.)	75,000	5,700
35	29,000	1,300
50	14,000	400
100	2,000	43
150	400	10

* Derived from graphs on pp. 21 and 23 of the Seafood Consumption Study, September 1973--August 1974 by the National Purchase Diary, Shaumburg, Illinois, 1975. Sponsored by the Tuna Research Foundation.

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another hypothetical case, if the PCB level in tuna should ever reach 1 ppm, then about 5,000 tuna fish consumers, those who eat in excess of 175 g/day, would exceed the 200 mcg/day limit from tuna alone.

Survey data do show that in general U.S. fish eaters include a wide variety of fish items in their diet. Thus, even if certain items contain toxic micro-constituents at or near FDA guideline level, the great majority of consumers would receive only a small fraction of their average dietary intake from these sources.

Clearly, there is a need for demographic information, similar to that available on total fish and tuna, on the other principal foodfish items in the U.S. diet; and a need to extend and better measure the high-consumption tail of the distributions, to get a correct picture of the number and type of consumers eating in excess of 100g/day of any single fish product.

IV. Conclusions

At present, it is difficult to estimate human exposure to PCB from eating fish, either for the population as a whole or for subgroups at higher risk. Fragmentary evidence suggests that the exposure to the population as a whole from PCB residues in ingested fish is probably well below 19 mcg/day-consumer, based on PCB levels which are probably well below 1 ppm and 19g fish consumed/day.

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Although it is important to know the total population exposure, the first priority should be given to defining the dietary intake of PCBs in special subpopulations at high risk by reason of high consumption of fatty fish, or high sensitivity to the toxic action of PCBs. Such populations might include pregnant women and young children, dieters, low income groups and sport fishermen living in coastal and lake regions where there is known PCB contamination. Primate studies suggest that pregnant women and young children will be particularly sensitive to PCBs, and dieters, and in some areas low income groups may rely heavily on fish for food. For each subpopulation, the amount and kind of fish in the diet and the PCB residue levels in the fish eaten must be obtained in order to determine exposure. None of the necessary information to define the human PCB exposure in subpopulations is presently known.

The first priority in systematically monitoring and analyzing for PCB residues in fish should therefore be among the oily fish such as salmon, trout, mackerel, shad, sardines, herring, bluefin tuna, sable fish, white fish, striped bass, and bluefish, that have been identified as significant food items in the diets of special subpopulations of consumers.

Although only minimal dietary exposure to PCBs may occur through food, there is evidence of potentially significant exposure

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in those sub-groups of the population who regularly consume freshwater fish from waters which are contaminated with PCBs at levels which exceed the FDA temporary tolerances. These sub-groups of the population would include sports fishermen and others who consume locally caught freshwater fish.

In surveys conducted by the State of New York and FDA, samples of 17 species of fish were collected from 10 points on the Hudson River between Glens Falls and Alpine, 13 samples were collected at Glens Falls and 68 samples below Glens Falls. The data from these surveys indicate that 53 out of 68 samples of fish collected at or below Fort Edward (approximately 7 miles below Glens Falls) contained PCBs in excess of 5 ppm. The average level of PCB contamination in these 68 samples was 31.3 ppm. In contrast, only trace levels were found in the 13 samples obtained at Glens Falls. A high proportion of finfish and eels from all sampling points below Glens Falls contained PCB levels in excess of 5 ppm. The Fort Edward sampling point had the highest levels for the species examined, with individual samples ranging from 20.1 to 178 ppm.

Twenty-eight of the 33 samples of coho and chinook salmon from Lake Ontario exceeded 5 ppm, with a range from 21 ppm to 24.6 ppm. Of the 4 samples of lake trout tested, results were in the range of 10 to 15 ppm. All other species of fish sampled from Lake Ontario were at 5 ppm or less PCBs.

The Great Lakes represent another area of the nation contaminated with PCBs. The Michigan Water Resources Commission has reported

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that many surface water samples contained PCBs at concentrations above the detection limit of 10 ppt. (10 significant levels of PCBs have been found in rivers and streams discharging into the Great Lakes. Effluents from wastewater treatment plants servicing industrialized communities have been found to be highly contaminated.

Sampling surveys of Great Lakes fish have shown that most species tested contained detectable levels of PCBs and that residue levels were generally proportional to fish size (age) and highest in the predator species. Except for whitefish, the species of commercial or sport interest (trouts and salmons) from Lake Michigan were found to be highly contaminated with PCBs. Data obtained from lake trout collected from various areas of Lake Michigan show mean PCB levels ranging from 3.06 ppm to 11.93 ppm.

The Michigan Department of Public Health has recently completed a study (Humphrey et al., 1976) which attempted to assess some of the consequences of human exposure to PCBs from the consumption of sportsfish caught in different areas of Lake Michigan. The study included exposed and control subjects from five areas of Michigan bordering on Lake Michigan. Exposed study subjects were those individuals who consumed at least 24 to 26 pounds of Great Lakes fish per year. Control subjects were those individuals who consumed less than six pounds of Great Lakes fish per year.

A preliminary assessment of the findings in the study indicate that the most frequently recorded quantity of fish consumed by the

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study participants was in the 24-25 pounds per year range. The highest recorded fish consumption over the two year period of the study was 180 pounds per year and the highest single season consumption was 260 pounds. Mean PCB levels in whole Lake Trout are reported as 18.93 ppm in 1973 and 22.91 ppm in 1974, and 12.17 ppm in Coho Salmon in 1973 and 10.45 ppm in 1974.

However, comparisons of PCB levels in raw vs. cooked fish indicate that actual human exposure to PCB from fish consumption is less than might be expected from the raw fish data. This is not unexpected since preparation (trimming away fatty tissue) and cooking have been shown to decrease the concentration of PCBs. For example, the PCB level in cooked Lake Trout consumed by the study participants ranged from 1.03 ppm to 4.67 ppm; in cooked salmon from 0.48 ppm to 5.38 ppm; and in other cooked fish from 0.36 ppm to 2.06 ppm. These levels are decidedly lower than the level of PCB contamination reported in raw trout and salmon.

PCBs were found in 501 blood and breast milk specimens collected from study participants during the study. The values ranged from a low of 0.007 ppm in blood in the control group to a high of 0.366 ppm in the exposed group. Although there was a wide range of blood values for each quantity of fish consumed, there was a highly significant correlation between the reported quantity of Lake Michigan fish consumed and the concentration of PCB in the blood of study participants. Using a natural log transformation

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of PCB values, the correlation between amount of fish consumed and PCB blood levels was significant ($t=6.24$, $p= 0.0001$), with higher reported fish consumption being associated with higher blood PCB levels.

No annual variation in PCB blood levels in humans could be demonstrated. The mean PCB blood values for the control and exposed groups did not appear to change markedly from 1973 to 1974. In addition, abstinence from Lake Michigan fish consumption for a period of 90 days or more did not change the PCB blood levels significantly. PCB blood levels over the abstaining period shows variation but no steady decline in PCB. In fact, more subjects showed no change or a rise than showed a decline in PCB blood levels over time.

The calculated quantity of PCB ingested by eating Lake Michigan fish averaged 46.5 mg/year and ranged from 14.17 to 114.31 mg/year. PCB ingestion for each individual was determined by proportioning the reported annual fish consumption by frequency of species eaten and the cooked fish PCB levels for those fish. The community average for cooked fish was used in instances were cooked fish determination were not available for a study participant. Because fish consumption was found to vary from year to year the average annual consumptic for each individual for the two baseline years of study was used in each case.

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Results from this study indicate the strong likelihood that the maximum allowable ingestion of 1 mcg/kg body weight/day recommended for protracted exposure to PCB is being exceeded by the majority of the exposed group participants, and by inference, by a substantial number of individuals participating in sport fishing and who consume quantities of contaminated fish. The calculated mean daily dose received by the exposed group is 1.7 mcg/kg/day and ranges from 0.49 mcg to 3.94 mcg/kg/day. If the average annual rate of PCB ingestion from fish indicated by these study results were continued over the years, and if net accumulation occurs, the average sports fisherman consuming contaminated fish could receive a total PCB dose equal to the 200 mg safety limit in approximately 4.3 years. Under the same set of assumptions, individuals consuming greatet than average amounts of contaminated fish would reach the total dose level sooner.

No adverse health effects or group of symptoms could be identified in the exposed group that were clearly related to PCB exposure. This implies that exposure to PCBs from eating contaminated fish at the levels observed and the presence of PCBs in these exposed persons has not caused any observable adverse health effects at the time of the study. However this does not exclude the possibility that effects too subtle for detection are occurring or the possibility of long-term adverse health effects.

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Considerable scientific interest has centered on the Yusho incident in Japan where in 1968 human intoxication with Kanechlor 400, a PCB manufactured in Japan, was noted when a heat exchange leaked this PCB into rice oil ("Yusho" oil) which was consumed by Japanese families.

The typical clinical findings included chloracne and increased pigmentation of the skin, increased eye discharge, transient visual disturbances, feeling of weakness, numbness in limbs, headaches and disturbances in liver function. Most of the babies born to mothers with Yusho had skin discoloration which slowly regressed as the children grew in size. Adult "Yusho" patients had protracted clinical disease with a slow regression of symptoms and signs, suggesting a slow metabolism and excretion of the PCB in humans, probably resulting from a long biological half-life.

A review of the literature extent in 1972 led to the following facts with respect to this tragic incident in Japan:

1. The average PCB content of the rice oil in the dose-response epidemiologic study was 2,500 ppm.

2. In this dose-response epidemiologic study, the average cumulative intake of PCBs, leading to overt symptomatology, was 2000 g. In this same study, the lowest dose leading to overt symptomatology was 500 mg.

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3. The toxicity seen was the result of the ingestion of the PCBs contaminant in the rice oil.

A summary updating of the "Yusho" incident was presented by Professor Kuratsune at the National Conference on Polychlorinated Biphenyls, Chicago, Illinois, November 19, 1975 (Kuratsune et al., 1976). This report affects the original conclusions enumerated above.

1. PCBs Content of "Yusho" Oil.

The first reported PCB determination was made on a canned contaminated rice oil produced on February 5, 1968, and whose consumption was associated with overt symptomology. One group of Yusho patients was associated with ingestion of this contaminated canned rice oil produced or shipped on February 5 and 6, 1968 (Kuratsune et al., 1972).

The detailed epidemiologic studies are given in the papers by Kuratsune et al., (1969) and Yoshimura (1971) and summarized in English by Kuratsune (1972), Kuratsune et al., (1971) and Kuratsune et al., (1972). Of 325 patients queried, 166 of 170 used canned rice oil produced or shipped on February 5 and 6, 1968, and 143 of 155 used bottled rice oil shipped from February 5 to 15, 1968. Tsukamoto et al., (1969) determined that the organic chlorine content of canned rice oils produced or shipped on February 5, 1968, was 1000 to 1500 ppm, by chemical and activation analysis. Since Kanechlor 400 had a 48 per

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cent chlorine content, if one attributed all the organic chlorine to this specific chlorinated biphenyl, then this canned rice oil contained, as an average, 2500 ppm PCBs. Kuratsune et al., (1969) reported that a qualitative GLC survey of 109 samples of bottled rice oil shipped between October, 1967, and October, 1968, showed "significant" PCBs content only in those samples between February 7 to 10, 1968. The largest amount was reported in the sample of February 7, 1968, but the quantity was not given. No bottled rice oil samples were available for February 5 and 6, 1968. However, in the paper by Kuratsune et al., (1971), the most marked contamination of bottled rice oil was for that shipped on February 7, 1968; and the maximum chlorine content was 462 ppm. One may assume that this number applies to the sample of bottled rice oil of February 7, 1968, giving this sample a PCBs content of 924 ppm. Kuratsune et al., (1976), reporting the work of Nagayama et al., (1975b), gives the PCBs analyses for three samples of toxic "Yusho" oil, used by three independent families with "Yusho", as approximately 800 to 1000 ppm. These were GLC/MS measurements. Nagayama, et al., (1975b), described these samples as follows:

"Rice oil used by patients with Yuso ("Yusho oil"): 3 samples of rice oil used by 3 independent families with Yusho in 1968. These samples had been kept in glass bottles with glass stoppers at room temperature in our laboratory until 1974 when the analysis was made."

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Kuratsune (1976) pointed out that these three samples were canned oil and considered to have been produced and shipped on February 5 or 6, 1968. This is also suggested in footnote a, Table 5, in the paper by Kuratsune et al., (1976). It was reported previously that, based on organic chlorine determinations, Tsukamoto et al., (1969) reported an average PCB content of the canned oil of February 5, 1968, to be 2500 ppm. Now, based on BLC/MS, we have a PCB content of ca 1000 ppm for canned oil sample of February 5 or 6, 1968.

What are the possible explanations for this discrepancy in values? One possibility is based on the assumptions associated with the method of measurement by Tsukamoto et al., (1969); namely, determination of total organic chlorine. Thus, any orgnic chlorine present in the rice oil, which was not a chlorinated biphenyl, would be included in the PCB analysis. Some possibilities include: chlorinated dibenzofurans, chlorinated naphthalenes, chlorinated paraffins, other chlorinated aliphatics and non-biphenyl aromatics.

Another possibility is related to the distribution, with time, of the contaminated rice oil samples. February 5, 1968, occurred on a Monday. The first rice oil samples reported to contain PCBs were produced on this date (Tsukamoto et al.; 1969). If the leak first occurred sometime over the weekend (February 3 and 4, 1968), and

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production was resumed Monday morning, February 5, 1968, then one would expect the samples of this date to be higher in PCB content.

Therefore, one would expect the first batches Monday morning to be highest with a dimunution of PCB content with time. Tsukamoto et al., (1969) reported the organic chlorine content of six canned oils produced Monday, February 5, 1968, as follows: 1020, 1170, 1070, 1080, 1030, and 1500 ppm. In the survey of bottled oils, Kuratsune et al., (1969) reported that for those samples where PCBs were found, the greatest amount was in the samples of February 7 (Wednesday); and after February 11. It was inferred from the paper by Kuratsune et al., (1971) that the PCB content of the bottled rice oil samples of February 7, 1968, was 924 ppm. In addition, in Table 5, Kuratsune et al., (1976) gave a value of 134 ppm PCB for a rice oil produced on February 10, 1968. Thus, the available data does confirm a diminution of PCB contamination of the rice oil with time. This is summarized below:

Date	Source	PCB content (ppm)	Method
Feb. 5, 1968	canned	2000-3000	organic Cl
Feb. 5 or 6, 1968	canned (?)	ca 1000	GLC/MS
Feb. 7, 1968	bottled	924	organic Cl
Feb. 10, 1968	bottled	134	?
After Feb. 11 1968	bottled	just detectable	GLC (?)

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The resolution of the varying PCB values for the canned oil cannot be made. However, Kuratsune (1976) confirmed that the production of rice oil had been suspended for an unknown period of time prior to February 6, 1968, when it resumed.

2. Dose-Response

There were 1291 "Yusho" patients as of April 30, 1975 Oeme, 1975). Of this total group, the dose-response relationship was developed from a detailed analysis of 146 patients (Yoshimura 1971; Kuratsune et al., 1972). These 146 patients all consumed contaminated canned rice oil produced on February 5, 1968 contained 2000 to 3000 ppm PCBs as Kanechlor 400 (Tsukamota et al., (1972) estimated that the lowest dose producing symptoms was 0.5 gm.

If the PCB content of this canned oil was ca 1000 ppm, as discussed in the previous section, then the average dose producing an overt effect was 0.8 gm. and the lowest dose producing an overt effect was 0.2 gm.

3. Causative Factors.

Originally, rice oil contaminated with a heat exchanger, Kanechlor 400, a polychlorinated biphenyl, was associated with "Yusho" symptomatology (see discussion in section

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1 above). PCBs were identified in the contaminated rice oil consumed and in the blood and tissues of Yusho patients. Therefore, the effects seen were attributed to PCBs.

In the review by Kuratsune et al., (1976), a new factor was introduced into the system; namely, the canned rice oil was also contaminated with chlorinated dibenzofurans to the extent of 5 ppm. In addition, in this same paper by Kuratsune et al., (1976), they presented data of Nagayama et al., showing polychlorinated dibenzofurans in the liver and adipose tissue of Yusho patients, while none was found in that of a control group. The ratio of PCBs to PCDFs in Kanechlor 400, a Yusho oil of February 5 or 6, 1968, in adipose tissue and liver from a Yusho patient were 50,000; 200; 144; and 4 respectively. Thus, relative to Yusho oil, the liver with a PCB/PCDF ratio of 4 to 1, appears to selectively concentrate PCDFs relative to PCBs.

Relative to PCBs, PCDFs are about 250 times higher in the rice oil than in Kanechlor 400 (Nagayama et al, 1975b; Kuratsure et al., 1976).[1] They also stated that PCDFs may be a factor in Yusho disease. In another

[1] It should be noted that we are comparing chlorinated dibenzofuran content of an unused Kanechlor 400 to that after prolonged use in a heat exchanger.

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paper Nagayama et al., (1975a) reported that it "is said that the toxicity of PCDF is said to be from 200 to 500 times that of PCB". At the lower factor (200), contaminated rice oil would be expected to be twice as toxic as Kanechlor 400. Also, in this same paper they stated that the symptoms seen in Yusho patients seemed to be more severe than would be expected just from the PCB intake associated with the oil.

If PCDF is 200 to 500 times more toxic than PCB (Nagayama et al., 1975a), then contaminated rice oil would be 2 to 3.5 times more toxic than that expected from its PCB content, alone. Kuratsune et al., (1972), estimated that if the average amount of contaminated rice oil ingested by a "Yusho" exposed person, is related solely in terms of its PCB equivalent, then the amount of oil needed to be ingested, on that basis, would be 1600 ml to 2800 ml. At a PCB content of 2500 ppm, this is an ingestion of 4 to 7 gm of PCBs equivalent; whereas at a PCB content of 1000 ppm, this is an ingestion of 1.6 to 2.8 gm of PCBs equivalent.

Conclusion

The complexities and uncertainties associated with the most recent reports of the "Yusho" incident in Japan, make it extremely difficult to quantify possible human health effects resulting from exposure to PCBs alone.

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V. Occupational Exposure to PCBs

The earliest reports of adverse health effects due to exposure of workers to PCBs in this country are probably those of Schwartz (1936) who described skin lesions and symptoms of systemic poisoning among workers who were said to have inhaled chloro diphenyls; their complaints included digestive disturbances, burning of the eyes, impotence, and hematuria. Patch tests with the chlorodiphenyls were negative, and Schwartz speculated that mechanical plugging of the follicles of the skin as the fumes solidified on it were responsible for the skin lesions; the chlorine present in the products were thought to then exert an irritating effect on the plugged follicles, and to thus cause suppuration. No quantitative data were reported, but a number of preventive practices were recommended.

There have been numerous reports over the ensuing years (Schwartz and Bartow, 1942), (Greenburg et al., 1939), (Drinker et al., 1937), (Good et al., 1943), (Schwartz, 1943) and (Meigs, et al., 1954) of cutaneous eruptions and of systemic manifestations (sometimes fatal) as well, among marine electricians, machinists, capacitor and transformer manufacturing workers, and others occupationally exposed to PCBs. However, in many of these reports the exposures are described as having been to mixtures of chlorinated hydrocarbons, quite often of chlorinated naphthalenes and PCBs.

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The skin lesions described by Schwartz (1936) have come to be designated generally as "chloracne." Chloracne can be produced by a number of chemical compounds, including chlorinated dibenzofurans and certain isomers of the chlorinated dibenzodioxins (Kimbrough, 1972). Oily skin and large pores seem to predispose to the disease, while the opposite is the case for smooth, tender skin (Kimbrough, 1974). Chloracne also has occurred among workers engaged in the production of 2,4,5-T (Poland et al., 1971).

Part of the chloracne lesion resembles adolescent acne, but it is generally more severe, and lesion distribution is inconsistent with, although it may be superimposed upon, adolescent acne. It is known that chloracne can be produced by either the systemic absorption of chlorinated biphenyls or the direct application of chloracnegenic compounds to the skin. Systemic effects sometimes result after occupational chloracne has manifested itself; these may include loss of appetite, nausea, edema of the face and hands, abdominal pain, vomiting, and burning and soreness of the eyes. No fully satisfactory explanations have been made of the development of chloracne. Chloracne is generally very persistent, and there is the preferred control measure. An excellent review of this subject is that by Crow (1970).

The U.S. occupational standards for PCBs are: 8-hour time-weighted average exposure limits of 1 mg/m^3 (skin) for the 42% chlorinated product, and 0.5 mg/m^3 (skin) for the 54% chlorinated product (CFR, Title 29, Part 1910.93). The National Institute for Occupational Safety and Health has under way the preparation of

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criteria for a recommended standard for occupational exposure to polychlorinated biphenyls. In addition to an environmental exposure limit, this document will provide comprehensive recommendations for medical surveillance, safe work practices, and engineering controls to ensure employee protection during occupational exposure over a working lifetime; it is scheduled for transmittal to the Department of Labor in late 1976 or early 1977. NIOSH also is undertaking certain studies of employee populations (mainly in U.S. capacitor factories) in order to better define the nature and extent of any chronic and/or life-shortening effects of exposure to PCB.

Practically all of the currently available information on worker health and PCB exposure is found in foreign literature. For example, Karppahen and Kolho (1974) reported on relationships between the concentration of PCB's in the blood of all, and in the adipose tissues of some, of 29 persons in "good health"* from

*Kolho has stated that the capacitor plant workers received quarterly health examinations, and, in addition to the clinical examination made at the time of the investigation, serum alkaline phosphatase, GOT, and GPT activities were determined; the 6 employees with the highest blood concentrations of PCBs also had BSP excretion tests performed. All results were normal.

In view of claims based on animal experiments that PCBs can induce liver microsomal enzyme activity, the authors also determined the half-time of antipyrin before and after phenobarbital induction (1 mg phenobarbital/kg body weight/day/3 days) for 6 capacitor plant employees and 6 controls; no enzyme induction was observed. Further, because of claims that PCB's have effects on steroid metabolism, 4 capacitor plant workers were tested for ACTH (serum, presumably); all results were reported to be within the normal range (letter from S. Hernberg to A. C. Kolbye, Jr., 12/23/75.

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three different employee groups in Finland. None of the employees had no history of occupational exposure to PCBs, six of them had handled PCB samples in an analytical laboratory, and the other eleven of them had been employed for 6 years in a capacitor factory where Aroclor 1242 was used as the impregnating fluid. It was stated that average PCB concentrations in the air of the capacitor factory had not exceeded "internationally accepted limits**," and that special attention had been given to skin protection.

Table 15 shows the observed tissue concentratins of PCB's; the authors were unable to detect any biological effects of the approximately 50-fold larger PCB concentrations in the blood of the capacitor plant employees, compared to the "unexposed" control group.

Ouw et al., (1974) conducted a survey to determine the degree of absorption and the health effects of exposure to "electrical grade" Aroclor 1242 (that "did not contain any impurities") for varying periods of time. PCB concentrations in the air of a capacitor factory in New South Wales, Australia*, were measured, and 34 occupationally exposed employees (15 males, 19 females, ranging in age from 33 to 55 years) were examined and compared with volunteer controls (23 males, 7 females ranging in age from 20 to 50

*The Joint ILO/WHO Committee on Occupational Health, in its sixth report (World Health Organization Technical Report Series No. 415, 1969), recommended for international adoption a "safe concentration zone" of 1 mg/m^3 for chlorinated derivatives of diphenyl.

**Aroclor 1242 is not manufactured in Australia (Ouw et al., 1974).

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TABLE 15

Concentration of PCB's

Subjects	In blood Fat basis mg/kg		In adipose tissue Fat basis mg/kg	
	Average	Range	Sample no	
Workers in capacitor factory	313	100-700	1	200
			2	11
			3	160
			4	285
			5	635
Persons handling PCB's in analytical laboratory	53	33-71	not analyzed	
Persons without any special exposure to PCB's	5.4	3.6-9.9	1	2.3
			2	1.5

From Karppanen and Kolho (1974)

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years) having no history of occupational exposure to PCB's. Study parameters included occupational and medical histories, PCB-in-blood concentration estimates, and liver function (serum bilirubin, alkaline phosphatase, total protein, and GPT, and BSP excretion) tests.

The authors noted that exposed workers tended to complain of eye, face, and skin "burning," that the PCB "'fume' ... has a pungent smell which often causes persistent body odour," and that the employees with higher blood concentrations of PCBs complained most often of the skin lesions (one case of chloracne, five cases of "an eczematous rash on" the legs and hands), although there apparently was poor correlation of blood PCB's with the severity of the complaints. No significant health effects were observed among those of the 34 workers whose blood PCB concentrations were below 200 ppb.

There was a statistically significant difference between the blood PCB concentrations of the exposed group and the control group (P less than 0.01). Table 16 shows the concentrations of Aroclor 1242 in the capacitor plant air prior to and after exhaust ventilation system "improvements" had been made. (The Australian National Health and Medical Research Council recommended (Atmospheric Contaminants, 1970) exposure limit values of 1.00 mg/m^3 for PCBs of 42% and 54% chlorine content, respectively). Table 17 shows that there was no lowering of blood PCB concentration among those workers tested two months after the installation of a more

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TABLE 16

Arocloro 1242 concentrations in the air inside capacitor plant before and after improvement of exhaust ventilation system

No.	Areas in the Impregnation Room	Aroclor concentration in mg/m^3	
		Before	After
1	Area in the unloading tank in front of exhaust register from operator's breathing zone	1.44	0.75
2	Area in the unloading tank not in front of exhaust register	2.22	0.7
3	General atmosphere near tank	1.08	0.18
4	Soldering area	0.32	0.08

From Ouw et al (1974)

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TABLE 17

Mean blood Aroclor 1242 levels before and after improvement of exhaust ventilation and the recommendation to use "suitable impervious" gloves.

Group	Mean blood Aroclor levels in ppb. Retention times relative to Aldrin I.		
	0.69	1.31	1.41
Before	281.6	135.1	58.41
After	477.2	225.4	524.7
Statistical differences	Not significant difference (P 0.01)	Not significant difference () 0.01)	Significant difference (P 0.05)

From Ouw et al (1974)

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efficient exhaust ventilation system and the concomitant recommendation to wear "suitable impervious gloves" in order to reduce PCB absorption through the skin. The authors suggested that a failure to adhere strictly to the glove recommendation might explain the continued elevation blood PCB levels. Another possibility might be that PCBs were continually mobilized from storage in adipose tissues.

The Japanese Ministry of Labor (Regulation for the Prevention of Disturbances due to Specified Chemical Substances, under the Act for Safety and Health of Workers, of April 28, 1971) established an occupational environmental exposure limit for PCBs of 0.5 mg/m^3 at 25° C, one atm (Ad Hoc Committee, 1974). Japanese importation of PCBs commenced around 1950, and early uses were as dielectrics in capacitors and transformers. In 1954, Kanegafuchi Chemical Industry Co., Ltd. started PCB production in Japan and it was at about this time that chloracne eruptions among workers were first reported. Slightly earlier (1953) incidents, however, were reported by Hara (1969), of changes attributable to PCBs in blood and urine findings among capacitor factory workers.

According to an Ad Hoc Committee sponsored by the Japanese Environmental Agency (1974), PCB concentrations in the air of a Japanese capacitor factory (where the major PCB constituent was "diphenyl pentachloride") were found to range from 0.37 to 6.75 mg/m^3; this was between the years 1953 and 1957, and prior to the

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date when the aforementioned occupational exposure limit was promulgated. The highest concentration was measured where PCBs were heated to drive out entrained/dissolved air. Admittedly, the analytical methodology for PCBs in those years was not as refined as that now in use, but it is thought likely (authors) that some employees were exposed continually at concentrations of several milligrams per cubic meter.

The Janapese literature is said to have contained no further reports on PCB-in-air measurements until the spring of 1972, just prior to the suspension of their usage. The production of PCBs was discontinued in Japan in June 1972, and their importation was discontinued in the following September. At that time Hasegawa et al., (1973) reported PCB measurements in the air of one PCB (Kanechlors 200-600) production plant (0.005-0.02 ppm), four capacitor manufacturing plants (Kanechlor 300 used) (0.01-0.05 ppm), and one plant where PCBs (Kanechlor 300) were used as a heat exchange medium (0.002 ppm). Peak values of 0.17 ppm and 0.67 ppm, respectively, were found in a capacitor plant "air-riddance" process area and in a capacitor impregnating area where tank leakage had occurred. Estimated (presumably 8-hour workday) time-weighted average exposures of affected employees were 0.02-0.03 ppm. Airborne PCBs in the capacitor plants were reported to consist of 70-80% vapor for material corresponding to Kanechlor 200, and of particulates larger than 0.1 micron for Kanechlor 300. The authors attributed the 3/1 vapor/particulate mix to selective evaporation of low boiling components of Kanechlor 300.

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Although no measurements were available, Hasegawa et al., (1973) estimated that environmental conditions in carbonless copy paper manufacturing facilities (using Kanechlor 300) were roughly similar to those found in capacitor factories. Beginning in February 1971, PCBs were phased out as the microcapsular solvent in this process, being replaced by "SAS" or KMC-oil;" however, during the period from November 1972 to January 1973, when occupational health surveys were being performed relative to SAS or KMC-oil toxicity, PCB concentrations of 0.013-0.4 ppb were measured in the environments of these facilities. General environmental concentrations of PCBs at that time were less than 0.0005 ppb, and outdoor PCB concentrations around the facilities were 0.0043 ppb (Hasegawa et al., 1973) and 0.009 ppb (Sato and Hasegawa, 1974). In an office room where carbonless copy paper was used, an air concentration 1.1 mcg PCB/m^3 was measured, and in the carbonless copy paper storage area of a post office, PCB concentrations of 8.7-21.1 mcg/m^3 were detected (Nishiyama et al., 1973).

The Japanese Ministry, in its "Regulations for Physical Examinations for the Prevention of Disturbances due to Specific Chemical Substances," promulgated on October 14, 1971, advised PCB users to examine employees for dermal andhepatic "symptoms" and their anamnesis, "subjective symptoms" such as anorexia and asthenia, and urine urobilinogen, in the first (pre-employment?) physical examination, and to "survey" working conditions, blood tests and liver function tests in the "secondary" (periodic re-?)

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examination. A 1973 notice adivsed those users of PCB's as heat exchange fluids to perform comprehensive health surveillance (Environmental Agency of Japan 1974). Yamamoto (1974) reported "positive" findings in 37 employees of 323 (total employment = 706 in 51 establishments) who were given "special" physical examinations in 1971.

Hara (1969) reported a 20-30% incidence of dermal "symptoms," consisting of "distinctive hair follicles" in exposed areas such as the face, neck, and forearm, and pimple-like skin eruptions of the face and neck, among employees in a capacitor factory that had been in operation between 1953 and 1963 (pentachlorobiphenyls) 1953-1957; Kanechlor 300, 1958-onward). No other, e.g., hepatic, dysfunction was observed, and no quantitative information was reported in the reference from which the preceding report was obtained; however, in a follow-up survey of workers in capacitor factories, Hara et al (1974) reported that by one year after the suspension of PCB usage skin findings had become milder.

Hasegawa et al., (1973) reported on a 1972 survey of capacitor factories, in which they noted that persons working in environments that contained 0.2-0.3 mg PCB's/m^3 (0.02-0.03 ppm) showed dermatolpgic ailments that included "brown chromodermatosis" of the dorsal joints of the hands and fingers and nail bed, and "acneform examthema." Several cases of comedo or acneform exanthema of the jaw, back, and thighs were seen also. These signs were no longer observed one month after the cessation of the handling of PCB's.

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In a factory where Kanechlor 300 was employed as a heat exchange medium, the environmental concentration of PCB's was reported to be 0.02/mg/m^3, and no dermal manifestations were observed among its employees (Hasegawa et al., 1973). Nor did Hashimoto (1974) observe any abnormalities among 236 workers in such a facility, to whom he administered "examination centered around liver function tests."

In 1972, when Hasegawa et al., (1973) performed a health survey of workers in carbonless copy paper factories, i.e., 2 years after the use of PCBs in such processes had ceased, they noted no dermal effects, and no liver function, blood, or urine test abnormalities were seen, with the exception of "slight abnormalities in lipid metabolism". PCB levels in the blood of these workers were reported as "approximately 0.01-0.02 ppm," or what amounted to a decrease to 10% of the levels during the period of PCB usage. The authors' data indicated that PCB's collected from the work atmosphere had apparently degraded to a product containing one less chlorine atom than the average number of chlorine atoms in the PCB's handled in the factory, and that, conversely, the PCB's found in the workers' blood contained one more chlorine atom than did the PCB's handled in the factory, i.e., if the PCB's found in the workers' blood were inhaled at the workplace, it can be surmised that the di- and trichloro- biphenyls disappeared rapidly from the body, whereas the tetrachlorobiphenyl was metabolized slowly.

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Hasegawa et al., (1973) concluded that blood analysis is a feasible method for determining body burdens of PCBs, and "probably more useful than the technique presently used by extracting adipose tissue and using it for PCB;" urinalysis for "PCBs did not appeal to them as a viable monitoring method. They noted, however, that there was no correlation between length of employment (and presumably, duration of exposure) and the amount of PCBs accumulated in the blood, i.e., with continued exposure, PCB levels in the blood did not increase linearly; in light of the demonstrated slow excretion rate of PCBs from the body, the authors conjectured that some different biotransformative mechanism comes into play after blood PCB levels exceed approximately 1 ppm (perhaps fat storage). This would seem to belie their confidence in blood analysis as a reliable index of exposure.

Kitamura et al., (1973) reported that the mean PCB level in the blood of 10 capacitor factory workers was 0.82 ppm (0.32-2.1 ppm) immediately after the cessation of PCB usage, and 0.31 ppm 3 months later, when almost all of the subject were observed to have skin signs. It seems significant that the blood PCB concentrations observed in this study were several fold higher than those seen by Hasegawa et al., (1973). Kitamura et al., (1973) attributed the skin effects to PCB's accumulated in the workers' bodies during the period of PCB usage. No other abnormalities were reported.

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Sagami et al., (1973) reported the case of a housewife in whom they observed skin effects several years after she had left 6 years of employment in a capacitor factory. She was found to have PCB concentrations of up to 0.13 ppm in her blood and of 42 ppm in samples her subcutaneous adipose tissue; this contrasted sharply with the findings of Hara et al (1974) that the blood PCB levels of 3 workers who remained at the same factory had decreased to 0.05 ppm and below, one year after the cessation of PCB usage (from levels of 0.05-0.3 ppm during the time of PCB usage (Hasegawa et al., 1973).

N.B. Some capacitor manufacturers in the U.S. use epoxide-type alkylating agents as additives to prolong the service life of PCBs. EPA sec. 308 responses from the General Electric Co., probably contain identifying data.

VI. Air and Water Exposure to PCBs

As indicated previously, nominal human exposure to PCB's in the U.S. population may occur from air and water. Samples of ambient air were collected in suburban areas of Miami, Florida; Jackson, Mississippi; and Fort Collins, Colorado. Preliminary results (Kutz and Yang, 1975) for samples taken in April, May and June of 1975 show that PCBs were present at all locations. Although the data varied, the average concentrations at each of the three locations was approximately 100 nanograms per cubic meter. Initial

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identification of the PCBs indicated that they were most comparable to the Aroclor 1254 standard.

Dennis (1975) has reported that data gathered from monitoring activities of surface waters and bottom sediments of the major drainage basins of the United States indicate the widespread occurrence of PCBs in both surface water and bottom deposits. A preliminary assessment of PCB levels shows mean residue levels in water ranged from 0.01 to 0.05 mcg/liter. The 0.05 mcg/liter were found in the South Atlantic Slope and Eastern Gulf of Mexico drainage basin. In general, the lowest PCB residue levels were found in drainage basins west of the Mississippi.

Kleinert (1975) has summarized the work completed by the Wisconsin Department of Natural Resources to identify some PCB sources in the environment in Wisconsin. Effluents from cooling water in aluminum foundries contained PCBs ranging from 11.5 to 335 ppb. Investigations revealed the common source to be leaking hydraulic fluids containing PCBs which were used in die cast machines. Effluents from paper mills that recycle wastepapers has measureable discharges ranging from 0.01 to 25 ppb.

Snow samples (Kleinert, 1975) were collected early in 1975. Analysis of the snow melt water from Racine, Kenosha, Madison, and Milwaukee revealed concentrations from 0.17 to 0.24 ppb. The author concludes that these values suggest that fallout of PCBs from the air may be a principal source of PCBs entering the waters

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of the State.

Hesse (1975) indicates that similar to the studies in Wisconsin, not all industrial effluents tested in Michigan contain measureable PCB levels. In testing over 900 industrial samples, approximately 40 percent contained PCBs above the 0.1 mcg/liter laboratory sensitivity limit. Twenty-three percent of the industries tested had greater than 0.5 mcg/liter, 18 percent greater than 1 mcg/liter, 6 percent greater than 10 mcg/liter and 2 percent greater than 100 mcg/liter.

Although much of the PCBs entering municipal waste treatment facilities are removed and become incorporated into the waste sludge, a sampling of 58 municipal wastewater treatment plant effluents throughout Michigan in 1973 showed an average concentration of 0.52 mcg/liter. Concentrations of PCBs are much higher in the sludges. The average for all plants was 15.6 mg/kg with individual values as high as 350 mg/kg. Since sewage sludges are commonly disposed of by incineration, spreading on agricultural land, or placing in landfills, the addition of PCBs to the environment is obvious.

VII. Residues of PCB's in Human Tissue and Milk

Yobs (1972) reported that 31.1 percent of 637 samples of human adipose tissue collected from the general population as part of the Human Monitoring Survey during 1971 were positive for PCBs in measureable amounts. These samples were collected in 18 states

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and the District of Columbia and positive samples were obtained from each of the sampling states and District. The percentage of PCB levels ranged from 34.2 percent non-detected, 33.3 percent less than 1 ppm, 27.3 percent 1-2 ppm and 5.2 percent greater than 5.2 ppm.

Kutz and Strassman (1975) have described the results of PCB monitoring during fiscal years 1973 and 1974 in which 35.1 percent and 40.3 percent, respectively, of the tissues collected contained levels of 1 ppm or more of PCBs on a net-weight basis. Analysis of the tissue revealed that the compounds found in adipose tissue were most comparable to those prevalent in Aroclor 1254 and Aroclor 1260. Additional analysis indicated that the most frequently encountered PCB residues were petan-, hexa-, and heptachlorobiphenyl compounds.

Residues of PCBs have also been detected in a study of human milk collected in Colorado where 8 or 40 samples contained residues ranging from 40 to 100 ppb (Savage et al., 1973).

A study of adipose tissue samples collected at autopsy from Canadians (Grant et al., 1975) indicates that the majority of Canadians have adipose tissue residues of 1 to 2 mg/kg of PCB. All adipose tissues had detectable levels of PCBs and 30 percent of the samples had PCB residues greater than 1 mg/kg with a range

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of 0.11 to 6.60 mg/kg. PCB residues in human milk from Ontario residents were found to be approximately 1 mg/kg on a fat basis.

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HUMAN EXPOSURE TO THE POLYBROMINATED BIPHENYLS

I. Introduction and Background

The polybrominated biphenyls (PBBs) in this report refers to either Firemaster BP-6 or hexabromobiphenyl manufactured by Michigan Chemical Corporation for use as a flame retardant for thermoplastics. This product is a mixture of brominated biphenyls with an average bromine content equivalent to about six bromine atoms per biphenyl molecule. Firemaster BP-6 is a mixture of the following brominated biphenyls[1]:

Tetrabromobiphenyl 2.0%

Pentabromobiphenyl 10.6%

Hexabromobiphenyl 62.8%

Heptabromobiphenyl 13.8%

Other bromobiphenyls 11.4%

The Michigan Chemical Corporation has stated that to their knowledge Firemaster BP-6 is the only polybrominated biphenyl produced in commercial quantity in the U.S. Their production estimates are:

Year	Pounds
1970	20,000
1971	200,000
1972	2,300,000
1973	3,900,000
1974 (Projected)	4,800,000

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Firemaster BP-6 has been used as a flame retardant in the manufacture of typewriter, calculator and microfilm reader housings, radio and TV parts, miscellaneous small automotive parts and small parts for electrical applications. The use of Firemaster BP-6 has been restricted to those applications where the end-use product is not exposed to either animal feed or food and there is no known use in flame retarding fabrics where human exposure would occur (1).

The ultimate disposition of Firemaster BP-6 upon burial is uncertain. The Michigan Chemical Corporation has stated that in their opinion this material will eventually undergo oxidative/biological degradation forming carbon dioxide, water and bromide ion (1).

II. Human Exposure

In October of 1973, adverse health effects were observed in cattle in several dairy herds in the State of Michigan. At that time, the cattle refused to eat manufactured feed; milk production decreased; there was a loss in body weight and the cattle developed abnormal hoof growth with lameness; cattle and swine aborted; and farmers reported the inability to breed heifers after they consumed feed manufactured by Farm Bureau Services. A herd of some 100 head of cattle sent to slaughter during this time period. exhibited enlarged livers.

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Analysis of samples of the suspected feed by laboratories of the U.S. Department of Agriculture at Beltsville, Maryland, revealed that the feed was contaminated with a flame retardant chemical, hexabrominated biphenyl. Subsequent investigation revealed that the Michigan Chemical Corporation manufactured magnesium oxide, a dairy feed supplement sold under the tradename Nutrimaster, and a flame retardant, hexabrominated biphenyl, sold under the tradename Firemaster BP-6. Both of these products were distributed in brown paper bags with either the name Nutrimaster or Firemaster stenciled across the top of the bag. When the top of the bag was torn off and discarded, identification was essentially lost.

As the result of a mix-up in bags, Firemaster BP-6 was mixed with animal feed in place of the Nutrimaster, apparently in the same proportion of use for the Nutrimaster. It appears that three kinds of feed were initially involved in this episode with PBB levels as follows:

Feed No.	PBB (ppm)
405	2.4
410	1,790
407	4,300

Samples of milk collected from individual farms soon after the PBB was identified as the contaminant ranged from 2.8 ppm on

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a fat basis to 270.5 ppm on a fat basis. Other products seized and destroyed included:

Butter	Range 1-2 ppm
Cheese	1.4 - 15.0 ppm
Canned milk	1.15 - 1.62 ppm

It has been estimated that between the onset of contamination in the fall of 1973 and the establishment of the quarantine of affected herds and flocks in the spring of 1974 over 10,000 Michigan residents have been exposed to PBB through the consumption of contaminated milk, meat and other dairy products. A considerable amount of variation in exposure has proabably occurred in both length of exposure and levels of exposure. As a group, the farm family members have been at greatest risk followed by those individuals who purchased dairy products from contaminated farms on a regular basis.

In order to determine whether or not persons exposed to PBB-contaminated products had suffered any acute adverse health effects, the Michigan Department of Public Health undertook a series of studies in the summer and fall of 1974. Study participants for the exposed group were dairy farm residents from farms which had been quarantined by the Michigan Department of Agriculture. The exposed subjects were limited to those who had lived or worked on the quarantined dairy farms for more than six months since May

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of 1973. Non-exposed subjects were randomly selected from a list of dairy producers in the same geographical area where farms had not been quarantined.

A total of 298 persons were interviewed in the study and physical examinations and/or blood samples were obtained for 110 persons in the exposed group and 104 persons from the control group.

The Michigan Department of Public Health has reported (1975) that responses to a set of 24 specific medical conditions revealed that none of the health complaints occurred consistently in either of the study groups. Statistical analysis showed that none of the listed complaints was significantly more frequent in those persons with the highest PBB levels when compared to other study subjects. Physical examinations of adults and children showed no unusual abnormalities of the heart, liver, spleen or nervous system. Urinalyses and complete blood counts did not reveal a significant excess of unusual abnormalities related to exposure or PBB levels.

These studies showed that blood levels of PBB were significantly higher in the study subjects from quarantined farms as compared to those from the non-quarantined farms; although some subjects from the farms showed low PBB blood levels (Table 18).

Several exposed females delivered normal babies without complication. Tests showed concentrations of PBB in breast milk to be considerably higher than that found in paired blood plasma (Table 19).

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Table 18

Distribution of PBB Blood Levels, Michigan, 1974

PBB Blood Levels (ppm)	Quarantined Farms Adults No.	%	Children No.	%	Nonquarantined Farms Adults No.	%	Children No.	%
0	3	3.7	-	-	21	28.4	-	-
0.002 - 0.019	43	52.4	8	28.6	52	70.3	29	96.7
0.020 - 0.090	19	23.2	10	35.7	1	1.4	1	3.3
0.100 - 0.490	11	13.4	3	10.7	0	0	0	0
0.500 - 2.260	6	7.3	7	25.0	0	0	0	0
TOTAL	82	100.0	28	100.0	74	100.1	30	100.0

Table 19

Comparison of PBB Concentrations In Human Breast Milk and Blood Plasma

Date	PBB Levels (ppm) Breast Milk	Blood Plasma
12/74	10.800	.082
6/74	22.700	.252
10/74	1.800	.014
3/75	.210	.003
3/75	92.660	1.068

Paired samples of adipose tissue and blood were collected in a group of 13 individuals entering the hospital for surgical procedures. The concentration of PBB in adipose tissue ranged from 61 to 370 times the PBB value found in blood plasma with an average ratio of 175 to 1 (Table 20).

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TABLE 20

Comparison of PBB Concentrations in
Human Adipose Tissue and Blood Plasma

Date	PBB Levels (ppm) Adipose Tissue	Blood Plasma
11/4	.410	.002
6/74 - 1/75	1.400	.005
3/75	3.000	.012
3/75	174.000	1.068
3/75	.248	.002
3/75	.274	.003
4/75	.177	.003
4/75	.152	.003
4/75	1.140	.004
4/75	.808	.004
4/75	.530	.007
4/75	.210	.003
5/75	1.110	.003

Reports of health complaints such as numbness, stomach pain, headache, fatigue and anxiety continue to be reported in the various newspapers in Michigan. Reports have also appeared in the press that several physicians in Michigan have reported abnormal liver function tests in patients exposed to PBB. Attempts to verify these reports with physicians have been unsuccessful.

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PCBs IN THE UNITED STATES INDUSTRIAL USE AND ENVIRONMENTAL DISTRIBUTION

TASK I

FEBRUARY 25, 1976

FINAL REPORT



U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

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PCBs IN THE UNITED STATES INDUSTRIAL USE AND ENVIRONMENTAL DISTRIBUTION

Task I

EPA Contract No. 68-01-3259

EPA Project Officer: Thomas Kopp

For

Environmental Protection Agency

Office of Toxic Substances
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REVIEW NOTICE

This report has been reviewed by the Office of Toxic Substances, EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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ABSTRACT

This document presents the current state of knowledge about the production, usage, and distribution of polychlorinated biphenyls (PCBs) in the United States. The information presented is derived from detailed studies on the production and first tier user industries, the past and present generation and disposition of PCB-containing wastes, environmental transport and cumulative loads, potential alternatives to PCBs usage, inadvertent losses to and potential formation in the environment, and current regulatory authorities for PCBs control. These results indicated that, although PCBs content of industrial wastes can be reduced through various approaches (treatment, substitution, etc.), there exists a potentially severe future hazard in the form of large amounts of PCBs currently contained in land disposal sites. Further definition of this and other aspects of the PCBs problem, and determination of ways to minimize the hazard, are recommended.

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SECTION I
INTRODUCTION

1.0 OVERVIEW OF THE PCBs PROBLEM

The term polychlorinated biphenyls (PCBs) refers to a family of organic chemicals which have been produced and marketed in this country for 45 years as a series of relatively complex mixtures under the trade name Aroclor. Each of these mixtures contains a number of chlorinated biphenyl isomers out of an overall range of chlorine content from one chlorine to ten chlorines per molecule. In general, higher chlorine content corresponds to greater resistance to chemical (and biochemical) degradation.

PCBs are among the stable organic compounds known, and, in addition, they exhibit other properties which render them extremely advantageous for use as dielectric and heat transfer fluids. These properties include low solubility in water, low vapor pressure, low flammability, high heat capacity, low electrical conductivity, favorable dielectric constant, and suitable viscosity-temperature relationships. Because of these properties, and also because PCBs exhibit little acute toxicity (toxic effects from high level, short term exposure), this family of materials has been extensively used in many industrial applications, primarily in "closed" or "semi-closed" systems such as electrical transformers and capacitors, heat transfer systems, and hydraulic systems. Most of the PCBs marketed to U.S. industry are still in service, primarily in electrical equipment. The remainder has entered the general environment; a significant fraction of this amount is present in air, water, soil, and sediment, but most of the PCBs in the environment are believed to be in landfills and dumps across the country.

In the late 1960's it became apparent that, although PCBs exhibit little acute toxicity, they are accumulated in the tissues of many biological species and do exhibit chronic (long-term) toxicity to many species even when the exposure is to very low concentrations. The effects of chronic PCB exposure may be considered as roughly comparable to those of DDT.

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The recognition of this problem resulted in a major program designed to lessen the environmental stress arising from widespread use and dissemination of PCBs; by mid-1971, the Monsanto Industrial Chemicals Co., the sole U.S. producer, had voluntarily terminated sales of Aroclors (PCBs and polychlorinated triphenyls, or PCTs) for all but closed electrical systems uses. Monsanto also, in the same time frame, offered incineration services for waste liquid PCBs and terminated production of the most highly chlorinated Aroclors.

During 1972 and 1973, the Food and Drug Administration developed limitations on PCBs concentrations, designed to eliminate interstate transport of PCB contaminated foodstuffs, for a number of important dietary items and packaging materials used for foods. These limitations also reinforced the elimination of PCBs usage in the U.S. except for closed electrical systems.

After approximately five years of the voluntary industrial restrictions, and about three years following the FDA limitations, a National Conference on PCBs was held in Chicago during November, 1975, under the joint sponsorship of EPA and other Government agencies. By that time it had become apparent that, although dietary intake of PCBs had declined (apparently as a result of the FDA actions plus cooperation of the food and food packaging industries), improved analytical techniques plus more extensive monitoring efforts had revealed PCBs contamination at environmentally significant levels to be more widespread than originally thought.

Results presented at the Chicago meeting indicated PCB levels in the environment, on an overall basis, to have been more or less constant since 1971, although there were local instances of both increases and decreases in PCB levels. It thus appears that, unlike DDT, elimination of PCBs from dissipative uses has not resulted in a significant reduction in environmental load.

2.0 OBJECTIVE AND SCOPE OF THE REPORT

It was against the above background that the work upon which this report is based was performed. The objective of this report is to present the current state of knowledge about PCBs production, distribution, usage, and losses to

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the environment in the United States. Many, but not all, of the facets of the PCBs problem are addressed; many of the estimates presented are based on engineering and scientific judgement instead of hard data, simply because hard data in these areas are not available. We hope that all assumptions and judgements in the report are clearly identified as such, and that sufficient supporting information, where available, is presented to justify the choices made.

While this report attempts to shed some light on the possible reasons why PCB levels in the environment are not decreasing as rapidly as had been hoped, its scope also includes a detailed presentation of past and present production and usage of PCBs in the United States, an analysis of PCB distribution and environmental transport as applied to Lake Michigan, a treatment in detail of potential substitutes and use alternatives, a discussion of the technical aspects of substitution, and discussions of various other aspects of the overall problem. Toxicological and human health aspects are not addressed; nor are the various current activities of EPA, other Government agencies, and individual states toward reducing entry of PCBs into the environment.

The information and data contained in the report were collected from personal interviews and telephone conversations with representatives of many of the firms handling or using PCBs, from trade associations, from the open literature, and from local, state, and Federal Government personnel, researchers, and other parties having interest in and information concerning the PCBs problem. Ten visits to plants were made; these covered the categories of PCBs production, small and large capacitor manufacturing, transformer manufacturing, investment casting, and waste disposal contracting (waste PCBs). The degree of cooperation, and therefore the accuracy of the data obtained, varied widely from industry to industry. Electric utilities provided key information, as did also other users or distributors of products containing PCBs.

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SECTION II

SUMMARY

1.0 PRODUCTION, USAGE, AND DISTRIBUTION OF PCBs

1.1 Overview of PCBs Industrial Usage in the United States

Over the past four years the domestic production and use of polychlorinated biphenyls (PCBs) have been approximately constant with averages of 40 million pounds per year for production and 33 million pounds per year for domestic sales. During this period Monsanto Industrial Chemicals Corp., the sole domestic producer, has supplied approximately 99 per cent of the domestic market. Monsanto sells several PCB mixtures under the generic trade name Aroclor, and purchase has been limited to intended use in nominally closed electrical systems (transformers and capacitors) since 1971 under voluntary restrictions imposed by Monsanto.

The remainder of the domestic usage depends on imported PCBs, most of which originate in Italy and the remainder in France. Decachlorobiphenyl is imported from Italy for use in investment casting wax, and the material imported from France is used in cooling systems of mining machinery.

Of the domestic sales of PCBs, 65 to 70 per cent are to manufacturers of capacitors, and the remainder to manufacturers of transformers. Transformers, which contain 2,000 to 2,500 pounds of PCBs on the average (present as a 60 to 70 per cent component of mixtures with trichlorobenzene called Askarels) are used primarily to change voltages during the transmission and distribution of electrical power. Approximately five per cent of the transformers in service in this country contain PCBs; most transformers contain mineral oil instead of PCBs. Capacitors containing PCBs are of two general types; small capacitors which are built into electrical appliances such as fluorescent lights, TV sets and small motors, and large capacitors which are used as separate units in electrical power distribution systems and with large industrial machinery such as electric motors and welding machines. PCBs are used in about 95 per cent of U.S.-produced liquid impregnated capacitors (most small capacitors in radios and other electronic equipment are solid-state units).

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PCBs are typically used in transformers where protection against fire is of paramount importance. Use of PCBs in capacitors is based on a number of factors, but fire protection and service life appear to be the most important. Industry codes, such as the National Electrical Code, specify the use of PCB-filled transformers and capacitors under a number of conditions. These codes will serve as institutional barriers to rapid reductions in PCBs usage, but at present there are also technical barriers to substitution of other materials for PCBs in electrical equipment.

The above overview of current PCBs usage in the U.S. is summarized by Figure 1.0-1, which traces domestic PCBs production and importation through first tier usage and distribution of PCBs - containing products.

1.2 Cumulative PCBs Production and Usage in the United States

Estimates developed for total PCBs production and utilization in the U.S. since their introduction to industry in 1929-30 are presented in Table 1.2-1. These data define the estimated proportions of PCBs used in various applications, and an accounting, based on available data plus estimates, of the current distribution of this material. Of the roughly 1.25 billion pounds purchased by U.S. industry, it is estimated that only 55 million pounds, or 4.4 per cent, have been destroyed by incineration or by degradation in the environment. About 60 per cent of the total domestic sales is still in service, almost all in capacitors and transformers. The remainder, about 44 million pounds, are in the environment; it is estimated that 290 million pounds are in landfills or dumps and 150 million pounds are "free" in the general environment (air, water, soil, sediments) and presumably available to the biota.

Some of the values in Table 1.2-1 are relatively well-established, while others are gross estimates resulting from a lack of data in the area. The estimated reliability for each value presented is shown on the table. For instance, the PCBs usage in carbonless copy paper is a firm value obtained from the only producer (NCR), where as the amount of PCBs environmentally degraded could conceivably range from a low value to the total of mono-, di-, and trichlorobiphenyl utilized but not still in service. The value for U.S. production could not be

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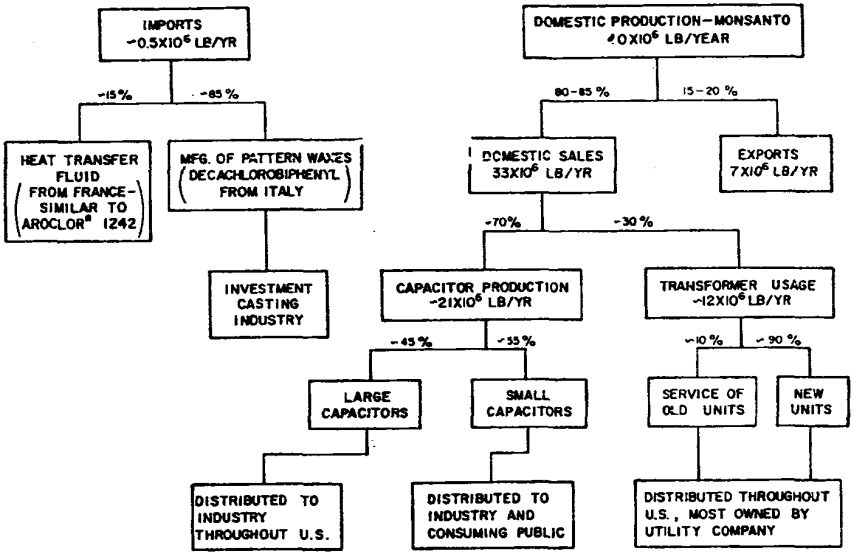

FIGURE 1.0-1. U.S. PRODUCTION AND USAGE OF PCBs SUMMARY OVER 1972--75

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Table 1.2-1

Estimates of Cumulative PCBs Production, Usage, and Gross Environmental Distribution in the United States Over the Period 1930-1975 in Millions of Pounds

	Commercial Production	Commercial Sales	Industrial Purchases of PCB	PCBs Currently in Service	PCBs Currently in Environment	PCBs Destroyed	Estimated Reliability of Values
U.S. PCB Production	1,400						+ 5% - 20%
Total U.S. PCB Imports	3						± 30%
U.S. PCB Domestic Usage		1,253					+ 5% - 20%
Total U.S. PCB Exports		150					± 20%
PCB by Use Category:							
Petroleum Additives			1				± 50%
Heat Transfer			20				± 10%
Misc. Industrial			27				± 15%
Carbonless Copy Paper			45				± 5%
Hydraulics and Lubricants			80				± 10%
Other Plasticizer Uses			115				± 15%
Capacitors			630	450			± 20%
Transformers			335	300			± 20%
Uses Other than Electrical				8			± 60%
PCB Degraded or Incinerated:							
Environmentally Degraded						30	± 70%
Incinerated						25	± 10%
Landfills and PCBs in Dumps:							
Cap. and Trans. Production Wastes					110		± 20%
Obsolete Elec. Equipment					80		± 40%
Other (paper, plastic, etc.)					100		± 40%
Free PCBs in the Environment (soil, water, air, sediment)					150		± 30%
Total	1,403	1,403	1,253	758	440	55	

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much over 1.45 billion pounds nor less than 1.1 billion pounds, based on analysis of other available or estimated data; hence, the estimated confidence interval for this value on Table 1.2-1 of +5 per cent and -20 per cent.

One of the more important conclusions from this work is the estimation of about two times the amount of PCBs in landfills and dumps as compared to the amount of PCBs already free in the environment. The material in land disposal sites may be considered a threat to become widely dispersed over a long period of time. The length of time required can only be guessed at, but is probably short in comparison to the time required for degradation of the PCBs by natural processes. Thus, release of the land disposal material through slow vaporization and leaching could very well worsen an already severe environmental problem.

1.3 Current Distribution of PCBs Usage and Associated Wastes

A material balance for PCBs production, sales, distribution, and wastes in 1974 is presented in Table 1.3-1. Reliability of the values were estimated as for the previous table. The amounts estimated to be land disposed, totaling 1.18 million pounds, do not include land disposal of previously used PCBs. However, the amounts listed under scrap PCBs incinerated account for all PCBs incineration in the U.S. during 1974 at the recommended temperature-time conditions (> 2000°F; > 1.5 seconds residence time). Of the total of 2.61 million pounds incinerated, the Monsanto facility accounted for over half. Other companies currently providing incineration services include General Electric, Rollins Environmental Services, and Chem-Trol Pollution Services, but the total number of such facilities known to be available in the U.S. is six.

1.4 Land Disposal and Environmental Load

The 1.18 million pounds per year of land-destined wastes estimated above is only a small portion of the total PCBs entering landfills and dumps yearly; the current estimated yearly rate of PCBs entering land disposal sites is about 12 million pounds. The largest source of this material is capacitors which have failed or become obsolete, or which are contained in obsolete equipment. Other important sources are industrial solid wastes from PCBs production and first-tier usage, and the total of other (non-electrical) municipal and industrial solid wastes.

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Table 1.3-1

Estimated Production, Usage, and Losses of PCBs in the United States during 1974 in Millions of Pounds

	Production or Imports	Commercial Sales	Industrial Purchases by Category	Amount Disposed or Lost	Estimated Reliability of Values
Domestic Production	40.466*				± 10%
Total Imports	0.45				± 50%
Monsanto Domestic Sales		34.406*			± 10%
Exports		5.395*			± 10%
Import Sales		0.45			± 50%
From Mfg. Inventory, etc.		0.665*			± 10%
PCBs Usage by Product Category					
Capacitors			22.0		± 20%
Transformers			12.0		± 20%
Investment Casting Wax			0.4		± 20%
Other			0.05		± 70%
PCBs Disposal to Land (assume PCBs to be 30% of total solid wastes)					
From PCBs manufacture				0.03	± 50%
From capacitor industry				0.48	± 50%
From transformer industry				0.27	± 50%
From investment casting				0.4	± 30%
Incineration of Scrap PCBs					
From PCBs manufacture				0.52	± 15%
From capacitor industry				1.45	± 20%
From transformer industry				0.64	± 20%
Industrial Discharges to Water and Sewers (as PCBs)					
From PCBs manufacture				0.0011**	± 40%
From capacitor industry				0.0021**	± 60%
From transformer industry				0.0001**	± 60%
Spills during Transport				0.01	± 50%
Totals	40.916	40.916	35.45	3.80	

* From Monsanto data

** Developed from data supplied by industry. Most analyses for PCBs concentrations in industrial wastewaters are probably not more accurate than ± 50 per cent.

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The total current environmental load of "Free" PCBs was estimated to be about 150 million pounds. An analysis of environment load (Free PCBs) average chlorine content per molecule indicated that, if mono-, di-, and trichloro isomers were disregarded, the average chlorine content of Free PCBs would be within seven per cent of the value for Aroclor 1254.

1.5 Foreign Production of PCBs

Known current producers of PCBs besides the United States include the United Kingdom, Czechoslovakia, France, Germany, Spain, and the U.S.S.R. Japan was a producer until 1972. In 1973, total foreign production of PCBs is estimated at 43 million pounds, corresponding to a 50 per cent reduction since 1971. On this basis, the U.S. production appears to be about half of the world total. Usage of PCBs in all countries is expected to decrease further as a result of recent findings on adverse environmental effects and potential human health hazards from PCBs, and this usage is expected to be essentially confined to use in capacitors and transformers.

2.0 CHARACTERIZATION OF INDUSTRY PRACTICE AND WASTE HANDLING FOR THE PCBs PRODUCER AND MAJOR FIRST-TIER USERS

2.1 Manufacture of PCBs and PCB-Containing Capacitors and Transformers

PCBs are produced domestically only by Monsanto at Sauget, Illinois. The process involves the batch chlorination of biphenyl and subsequent separation and purification of the desired chlorinated biphenyl fractions. The degree of chlorination is determined by the contact time in the reactor. Depending on the distance and size of shipment, transport is via tank car, tank truck, or common carrier (drums).

There are 17 capacitor plants and 18 transformer plants utilizing PCBs in the United States. Manufacture of both types of units involves initial preparation of internal and external cases, filling with PCBs under vacuum, cleaning and degreasing, and performance testing. The greatest PCB wastes occur in the filling operations. Filling of small capacitors (less than 2 pounds of PCBs) and most large capacitors is performed in chambers holding many small capacitors or fewer large ones. The chamber and the capacitors are evacuated and then flood-filled with the PCB liquid. Excess liquid is removed from the chamber, the filled

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units are cleaned and sealed, and then the sealed units are degreased, painted, and tested. Transformers and the largest types of capacitors are filled individually after evacuation; this produces relatively less chance of PCBs loss than the flood-filling process.

Of the 38 plants in the above categories, 10 discharge their effluents into the water ways while the remainder discharge into the sewage treatment plants. All plants in these categories have discharges under heavy rainfall conditions. There are three types of waste materials generated at these plants that require treatment and proper handling in order to minimize the PCB into the environment. These are:

(a) Waste waters containing trace quantities of PCBs (10 to 500 ppb PCBs);

(b) Waste PCBs, scrap oils and small quantities of process water highly contaminated with PCBs; and

(c) Burnable and non-burnable solid materials contaminated with PCBs.

Quantitative estimates of these wastes are given below:

	Waste Loads, Daily Average		
	PCB Discharge in Waterways or Sewers	Land-Destined PCB Wastes	Scrap Oils to Incineration
PCB Manufacturer	3.06 lbs	301 lbs	1425 lbs
Capacitor Industries	5.86 lbs	4440 lbs	3968 lbs
Transformer Industries	0.17 lbs	Unknown	1750 lbs

The above waste loads represent current industrial practice. It may be assumed that, prior to knowledge of the adverse environmental effects of PCBs, much of the types of material currently landfilled or incinerated was not disposed of properly and thus entered the environment directly.

As yet, very little is being done at these plants to control air emissions. The general industry assumption is that the vapor pressure of PCBs is so low that there will be essentially no air contamination. A few facilities, however, were reported to be filtering and chilling exhaust air from PCBs impregnation areas,

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and plant personnel are beginning to realize that evaporation of PCBs may make a significant contribution to general contamination of the plant area.

Since most water used at these facilities is for non-contact cooling purposes, at most plants it is possible to significantly reduce the effluent volume by segregation of wastewaters, recycling and proper housekeeping measures. Most user plants and the PCB producing plants have already undertaken PCBs containment programs in order to minimize the entry of PCBs into the environment. While the emissions of PCBs to water are expected to decrease due to improved pollution abatement of waterborne wastes, the release of PCBs to air and land may increase. One potential source of increasing air emissions is the increase in incineration due to proper handling of wastes which were previously discharged into the waterways or sewers. The quantities of land-destined wastes are expected to increase due to improved housekeeping measures.

Rivers receiving PCBs discharges for a number of years vary greatly in PCBs content with time, apparently depending upon PCB content in storm water runoff and the degree to which contaminated bottom sediments are agitated and suspended. Whereever there have been PCB operations in the past, there are probably high concentrations in local waterways bottom sediments.

Over the past 45 years, waste PCBs from transformer and capacitor operations have been used as local road oiling compounds. Sometimes they were discarded in dumps adjacent to manufacturing facilities. These are sources of long term leaching of PCBs into waterways, particularly with storm water runoff.

2.2 Treatment and Disposal of Industrial Wastes Containing PCBs

A study was performed to determine and compare the methods available for the treatment of PCB-containing wastes from the PCBs production, capacitor manufacturing, and transformer manufacturing industry categories. A full treatment of this technology, including cost estimates for treatment, may be found in the Task II Report under Contract 68-01-3259. Much of the technical portion of this work is reproduced herein and summarized below.

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2.2.1 Incineration

The most advanced treatment technology in use is incineration. The PCBs manufacturer and one user have plant scale facilities capable of destroying PCBs with very high efficiency. There are at least two commercial services available, with four incinerator locations in the Eastern and Southern U.S., for PCBs incineration.

Incineration is primarily applicable to waste PCBs and scrap oils contaminated with PCBs. Incinerators for PCBs destruction have the capacity of "burning" some contaminated wastewater but, of course, the proportion of that water to the exothermic oil burning must be kept low. Only one commercial incineration service (Rollins) can routinely handle all kinds of PCBs contaminated transformer and capacitor components, sludges, fuller's earth and other solids, as long as they can be contained in a 47 gallon fiber drum. One PCB user company incinerates transformer internals for purposes of metal recovery.

Waste liquid PCBs and scrap oils (contaminated PCBs) are best handled, as a guideline, by high temperature (2000-2400°F) and long residence time (2-3 seconds) incineration. However, because of incinerator design variables, the conditions should be chosen in each case to lead to 99.999% destruction. The best incinerator combination for handling wastes from these industries is a rotary burner fired by a liquid burner, and followed by an afterburner and scrubber system for HCl and particulate control. The rotary burner can be designed to handle a variety of solid materials, and the liquid burner can handle both the oily and water type wastes.

2.2.2 Treatment of PCB-Contaminated Wastewater

There is no commercial scale wastewater treatment for PCBs removal being practiced beyond those of gravity settling of the heavy PCBs layers as a sludge from the bottom of sumps or tanks, and skimming of a contaminated oil-layer from the water surfaces.

Adequate methodology is available for those plants wishing to control the release of PCBs to the environment. Currently available technologies can

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be applied to the efficient removal of PCBs from wastes, or their destruction with the other wastes. The PCBs content of wastewaters can be lowered to the 1 ppb level or below by removal of solids (and oil layers, where applicable), followed by adsorption of PCBs onto carbon, macroreticular polymer resins or possibly other adsorbents.

Carbon adsorption is currently the best available technology for plant scale treatment of PCBs wastewaters. This conclusion is based on laboratory tests with PCBs in water, and on the long background of plant scale use of carbon adsorption for removal of organics from water.

Polymeric resins (AMBERLITES) were found in laboratory tests to be approximately as effective as carbon in removing PCBs from water. Further pilot scale testing is needed with this newer (than carbon) technology to accurately assess its potential.

Ultraviolet catalyzed ozonation was determined to be the best method, demonstrated on a laboratory scale, for destruction of PCBs in wastewaters when the streams occur in large volume, on a relatively continuous flow basis and with PCBs at the ppb concentration levels. This technology has the potential for conversion of PCBs to CO_2, H_2O and HCl. However, significant development and optimization work would be required before application of the process becomes practical. In addition, the potential exists for production of toxic degradation products by UV-ozonation.

Although still in the laboratory stage, catalytic reduction of PCBs offers the possibility of reduction to biphenyl and HCl; and catalytic oxidation is another process which offers a potential for destruction of PCBs to CO_2, H_2O and HCl.

It is believed that wastewater treatment systems employing activated carbon and possibly UV-ozonation could produce effluents which would be at or below the limits of detectability for PCBs with current analytical techniques. However, since no full scale systems for the treatment of PCBs are in operation at this time, this possibility cannot be confirmed.

MONS 052609

Unfortunately, no methodology is presently available which can guarantee "zero discharge" of PCBs to the environment. "Zero discharge" objectives can be best met now by eliminating discharge streams and developing recycle systems. All streams that are high in pollutants and cannot be treated for reuse, including rainwater runoffs, could be collected and incinerated under a "zero discharge" objective.

2.3 Characterization of the Investment Casting Industry

Investment casting is a lost-wax process by which metal castings which are of intricate shapes or which require close dimensional tolerances are mass-produced. The pattern wax, some of which contains PCB filler, is molded and then used to make a ceramic shell (investment) whose internal dimensions are those of the desired product. The wax is typically melted from the shell, and the shell is fired (sintered), which removes the last traces of the wax. Then molten metal is poured into the mold (shell) and cooled to form the castings.

There are currently 135 investment casting foundries and four major investment casting wax manufacturing plants in the United States. The Yates Manufacturing Company, Chicago, Ill., is the sole known U.S. supplier of decachlorobiphenyl (deka) waxes. The deka content is 30 per cent of the total wax by weight. Yates currently imports deka from Italy and manufactures between 1 and 1.5 million pounds of deka wax annually. Very little is known about the wax manufacturing process. Wax manufacturers are also believed to use polychlorinated terphenyls (PCTs) imported from France.

The major losses of the virgin and used waxes appear to occur during the dewaxing of the ceramic mold. The mold is fired in a furnace to set the mold and remove the wax. Depending on furnace conditions, the deka or PCT in the wax is either burned or released to the atmosphere. The magnitude of these emissions is not known.

Most foundries recover the drained pattern wax and reuse it several times. It is estimated that the purchased wax is used an average of 2.5 times. Little of the wax is destroyed in the process; therefore, it is considered probable that the investment casting foundries store or dispose of relatively large amounts of used PCB- or PCT-containing wax.

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2.4 Transformer Service Industry

Most servicing of transformers is performed by electrical repair shops rather than by the utility or the owner of the transformer. Thirteen companies were identified as offering transformer service at a total of 131 locations. Servicing of askarel-filled transformers may include the filtering of the askarel to remove degradation products and moisture or the replacement of the askarel with new liquid. PCB wastes include filter media, scrapped askarel, and miscellaneous solvents, rags, etc. The proper disposal of these wastes is specified by a voluntary NEMA standard. Liquid PCBs are incinerated in most, but not all, cases. The total usage of PCBs by the transformer repair industry is about 800,000 lb/year, or about seven per cent of the amount used to manufacture new transformers.

3.0 SUBSTITUTES AND USE ALTERNATIVES FOR PCBs

Potential substitute materials and use or process alternatives which would eliminate or reduce the current requirements for PCBs were investigated. Important points from this study are summarized below.

3.1 Substitutes for PCBs in Capacitors

PCBs (primarily Aroclor 1016) are currently used in almost all U.S.-made capacitors for AC service (liquid-filled capacitors) and are uniquely suited for this application because of their high dielectric constant, high resistance to current flow and electrical breakdown, chemical stability, and non-flammability. A number of different liquid materials now under development or testing have been proposed as substitutes for PCBs in capacitors, including phthalate esters, synthetic hydrocarbons, alkylated chlorodiphenyl oxide, alkylated PCBs, diaryl sulfones, and silicones.

Since each of these materials is relatively more flammable than Aroclor 1016, it appears that use of any liquid substitute will probably pose more of a fire hazard than use of PCBs. Vulnerability of capacitor manufacturers to liability for damages from capacitor failure is a major factor in industry acceptance of a substitute capacitor fluid. The conservative code structure now in force could also pose significant barriers to reduction or elimination of PCBs usage in

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capacitors. In addition, data on electrical performance, toxicity to humans, and environmental effects of the potential substitutes are not presently sufficient to allow meaningful comparisons with PCBs.

Dry AC capacitors (film-type) are in the development stage. These capacitors are significantly larger than liquid-filled capacitors and are limited to a maximum of 280 volts. Satisfactory dry film capacitors will not be available until there are two separate technological breakthroughs: 1) the development of a plastic film that combines a high dielectric constant with a low loss-tangent; and 2) the development of winding techniques that exclude all air from the winding of the capacitor.

Although it is considered probable that satisfactory substitutes for PCBs will be developed within the next 5 years, no such material is presently available and much additional research remains to be done. On the other hand, a significant portion of the large capacitors used by utilities, and some in industry, are situated out-of-doors. These could be replaced by capacitors containing a more flammable fluid without significantly increasing the risk of fire.

Although direct replacement of existing PCB-filled capacitors with units containing substitutes appears possible for many large capacitors, anticipated size differences will present severe problems in retrofitting. The new fluids also cannot be directly substituted for PCBs in existing capacitors. In addition, disposal of obsolete or replaced units will probably be in landfills for many years to come. It is probable that the best replacement scheme for capacitors, assuming cessation of PCBs production and use, would be use of non-PCB replacements as units become obsolete or fail.

3.2 Substitutes for PCBs in Transformers

Aroclors 1242 and 1254 are currently used in about five per cent of U.S.-built transformers; most transformers are cooled with mineral oil. Transformers filled with askarel (60-70 per cent PCBs) are often specified for use in buildings and in hazardous locations where minimization of the fire hazard is of paramount importance. The National Fire Code requires that oil-filled units, and askarel-filled units rated for service over 35 kV, be enclosed in fireproof vaults when

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used in buildings. For units below 35 kV, the higher cost (by 20 to 30 per cent) of an askarel unit is more than offset by the savings on vault construction.

Open, air-cooled transformers are limited to a clean, dry environments, but are being increasingly used in commercial buildings. Closed, gas-cooled transformers are more expensive than askarel units. Both of the above types have voltage limitations and much less overload capacity than the askarel-filled type.

Several substitute liquids have been suggested for use in transformers which are less flammable than the currently used mineral oil, but which are more flammable than askarel. The most promising are a silicone oil and a synthetic paraffinic hydrocarbon. These liquids are characterized as being self extinguishing - i.e., they do not continue to burn after being ignited by a momentary electrical arc. Proposals have been submitted to the National Electrical Code to allow the use of these self extinguishing materials under those conditions where askarels are presently specified. Because of the relative lack of service experience with these liquids, it is unlikely that these proposals will be accepted. The next Code revision (1978) will probably continue to recognize only askarel and "oil filled" transformers.

It is likely that the "self extinguishing" liquids will prove to be satisfactory alternatives to PCBs. Substantial experience on the performance of the liquids will be required before the code requirements will be changed to allow their use. The restrictive Electrical Code, which has been incorporated into the OSHA Standards, may act to inhibit the accumulation of this data and thereby act to postpone the general acceptance of these substitutes for PCBs.

The major conclusion from this portion of the study was that technically acceptable alternatives to the use of PCBs in transformers exist and that their use should not result in a significant increase in fire hazards from transformer failure. At present the selection of PCB (askarel) transformers appears to be based primarily on cost rather than technical considerations.

As with capacitors, direct replacement of PCBs in existing transformers would present potentially severe problems. These include the extreme difficulty of removing more than 90-95 per cent of the PCBs, even by repeated flushing with

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a compatible solvent (trichlorobenzene), and the requirements of incinerating such large quantities of PCBs and contaminated solvent.

3.3 Alternatives to Other PCBs Applications

On a preliminary basis, there appear to be no overriding technical (or institutional) barriers to the use of alternatives to decachlorobiphenyl filler in investment casting waxes. (This also appears to be the case for the polychlorinated terphenyls.) Potential alternatives include use of materials such as isophthalic acid as the filler and use of the new low-shrinkage unfilled waxes. A cost increase of about ten per cent is projected for each of the above alternatives.

Since the voluntary restriction by Monsanto in 1971 of PCBs sales for use in closed electrical systems only, PCBs have largely been eliminated from usage in hydraulic and heat transfer systems. Adequate substitutes were generally available at the time of the Monsanto restriction, and the present usage of PCBs (believed to be minor) should be replaceable by alternatives with minimal disadvantage.

4.0 SOURCES OF INADVERTENT ENTRY OF PCBs INTO THE ENVIRONMENT

4.1 Paper Recycling

Over the period 1957 to 1971, approximately 45 million pounds of Aroclor 1242 was used by a single producer (NCR) in the production of carbonless copy paper. Some fraction of this material has entered the paper recycling stream and is apparently a major source of observed PCBs contamination of effluents from the secondary fiber recovery industry. PCBs were also added to paper in inks and possibly in other additives; this material was probably Aroclor 1254.

Thus, in its effort to conserve resources profitably, the secondary fiber recovery (paper recycling) industry is inadvertently releasing previously used and "stored" PCBs into the general environment, primarily to water. Reliable estimates of the amounts of PCBs so released are not available, and, although the significance of this release should diminish as office files are emptied, the amounts remaining to be released are not known.

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Results from an analysis of PCBs entering Lake Michigan, discussed later in Section 5.0, indicate that, although there is a significant concentration of paper recycling activities in the area of this lake, the contribution of paper mills to the total PCBs input to Lake Michigan is small in comparison to atmospheric fallout. However, effluents containing amounts of PCBs which are very small compared to the total environmental load can be extremely important on a local basis, and further investigation of this problem is urged.

It should be noted that water usage in the paper recycling industry is high and effluent PCB concentrations are typically 5 to 10 ppb. The cost of PCBs removal would therefore probably be higher per unit of profit than for the other industry categories described herein.

4.2 Effluent Contamination by PCBs in Other Industries

High concentrations of PCBs were recently reported in effluents from a number of plants engaged in the manufacture of machinery and mechanical products. These measurements have not been verified to data. PCBs were, in the past, used extensively in hydraulic and heat transfer systems, in lubricants, and in paints and plastics, so that it is not inconsistent that effluents from the machinery manufacturing industry contain PCBs. PCB contamination of effluents is known to have occurred via slow release of old deposits in sewers and elsewhere, although industrial usage in semi-open applications is believed to be continuing at a low level.

4.3 Inadvertant Production of PCBs in the Environment

Three general types of reactions were considered as potential sources of inadvertent production of PCBs. Of the three, the one considered most likely to occur is chlorination of biphenyl in wastewater during treatment. This refers specifically to the discharge of wastewater containing biphenyl to a municipal sewer and the subsequent chlorination of the material in the treatment plant.

Biphenyl is used extensively as a dye carrier for the dyeing of synthetic fibers; in this application, much of the biphenyl leaves the process as waste. The estimated U.S. industrial usage of biphenyl is about 50 million pounds per year, of which at least half is used in dyeing operations. Although chlorination of

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biphenyl in sewage treatment appears likely, the extent of neither the initial chlorination nor further chlorination is known. Further investigation of biphenyl chlorination as a possible source of PCBs is recommended.

Chlorinated biphenyls have been produced by the decomposition of DDT, although this requires recombination of phenyl radicals from cleavage of two DDT molecules. Significant production of PCBs in the environment by this mechanism is considered unlikely. Formation of PCBs via chlorination of the product formed from the combination of two substituted benzenes is also considered of less potential significance than direct chlorination of biphenyl in wastewater.

5.0 TRANSPORT AND DISTRIBUTION OF PCBs IN THE ENVIRONMENT

A first order mass balance model was developed and used to study the transport and distribution of PCBs in the environment. The total environmental load of "free" PCBs was regarded as a "pool" of mixed PCBs. In applying the model, the pool was assumed to exhibit properties roughly similar to those of Aroclor 1254. The model was applied to Lake Michigan; the boundaries of the region studied were taken to be the drainage basin of the lake. Lake Michigan is a nearly closed body of water of sufficient size to allow averaging of properties and of sufficient interest that some pertinent data were available.

The estimated total input of PCBs to Lake Michigan (1973-1974) was 13,400 lb/yr, of which 1,600 lb/yr came from point sources (summation of industrial and municipal discharges reaching the lake), 6,400 lb/yr represented fallout directly onto the lake, and 5,400 lb/yr was derived from fallout on the drainage basin (assumed to be 50 per cent of total fallout on the basin). Thus, it is estimated that about 88 per cent of the PCBs currently entering Lake Michigan arise from fallout.

Application of the model produced the following cumulative values for the period 1930 to 1975 (input function assumed proportional to domestic sales):

Total input	1.49×10^5 lb
Total in solution	1.0×10^5 lb
Total in biota	3.64×10^3 lb
Total in sediments	1.7×10^4 lb

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Total in outflow	9.07×10^3 lb
Total evaporated	1.93×10^4 lb

Since degradation of PCBs in the lake was assumed to be zero, the closing of the material balance depended upon total evaporation from the lake being 1.93×10^4 pounds, or about 13 per cent of the total input. This value is in excellent agreement with values derived both from kinetic theory and from co-distillation theory; this result substantiates both the model form and the material balance above.

Average water and biota concentrations derived from the analysis (using a bioconcentration factor over water of 4×10^4) are, for recent years:

	Water Conc. (ppt)	Biota Conc. (ppb)
1960	1.60	64
1965	2.92	117
1970	5.35	214
1975	9.10	364

The above agrees well with available data on lake and biotic concentrations since 1970.

Mean residence times of PCBs in air and water, and the transport mechanisms which operate at the various phase interfaces, are very important to the understanding of environmental transport and distribution. Lifetime values are extremely sensitive to the assumptions required for their calculation (required because of the lack of adequate experimental data). Estimates derived from work by others range from 20 days to eight years for the average lifetime to fallout of airborne PCBs. Residence times to evaporation in Lake Michigan appear to be on the order of ten hours, based on theoretical calculations, whereas residence times to evaporation from sea water may be one to two orders of magnitude lower.

The picture of gross PCBs transport consistent with all of the above findings is the one dominated by air transport. Terrestial components, including fresh water, are partial sinks responding primarily to input from fallout. Losses are to evaporation and to rivers, which enter the oceans where further (possibly rapid)

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evaporation occurs. Degradation of PCBs, which was assumed to be zero in the Lake Michigan analysis, appears too slow to have a significant effect. Industrial and municipal effluents and air emissions are sources of both old and new PCBs; large amounts enter landfills and a small fraction enters the cycle through leaching and evaporation.

If the above is even partially correct, then one possible answer to the question of why the restriction on uses beginning in 1971 has not caused the hoped for diminution in PCBs distribution is as follows:

(1) The systems which cause concern with regard to PCBs (freshwater systems and associated biota) serve as sinks for PCBs;
(2) Other possible sinks are not available or are ineffective in retaining PCBs; and
(3) The environmental degradation of PCBs is too slow to be significant over a five year period.

Further work in many aspects of PCBs transport and distribution are needed in order to estimate the real magnitude of the future environmental problem from these materials. Such work should also assist in identifying potential methods for reducing the environmental load of PCBs.

6.0 REGULATORY ACTIONS ON PCBs

Four government agencies, the Monsanto Company and NEMA comprise the regulatory forces currently restricting the use and distribution of PCBs. EPA, OSHA, FDA and USDA have, between them, authority to regulate and monitor food levels, disposal into waterways, industrial housekeeping, and safety practices in the work place. Each of these available authorities has a limited focus and is inadequate to prevent more PCBs from entering the environment.

There are currently no regulations to restrict the importation of PCBs as a chemical for use in applications banned by the Monsanto Company. As a result, PCB is being imported by a few companies for use in several "open-end" or "nominally-closed" applications.

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Several producing nations have voluntarily limited sales of PCBs. Since 1972, Japan has banned production and importation of PCBs. The United Kingdom has barred sales of PCBs to all applications except usage as dielectric fluids, while Germany has lessened this restrictive measure to include use in heat transfer and hydraulic systems. Among non-producing countries, Sweden and Norway have stringent regulations. In Sweden, only the Environmental Protection Board can authorize the use of PCBs or compounds containing PCBs, while in Norway only the Ministry of Social Affairs can authorize the use of PCBs.

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SECTION III

CONCLUSIONS AND RECOMMENDATIONS

1.0 Conclusions

Conclusions which have resulted directly from the work reported herein are presentod below. Some of these have been discussed briefly in the preceding section, but each is believed to be justified by information contained in the text of the report and the appendices.

(1) It is estimated that approximately 1.25 billion pounds of PCBs have been sold for industrial use in the U.S. since initiation of production around 1930.

(2) Of this amount, at least 95 per cent are still in existence; most is in service in capacitors and transformers, but about 290 million pounds are believed to reside in landfills and dumps and about 150 million are believed to be "free" in the environment. The magnitude of these values indicates that there is a strong future threat from PCBs present in land disposal sites.

(3) In 1974, U.S. usage of PCBs sold by Monsanto, the sole domestic producer, was distributed between capacitor manufacture (22 million pounds) and transformer manufacture (12 million pounds). Imported materials amounted to about one per cent of U.S. industrial purchases of PCBs in 1974; about 400,000 pounds (of decachlorobiphenyl) were used in investment casting and and an estimated 50,000 pounds of new material were used in specialized heat transfer systems.

(4) Waterborne effluents from PCBs production and first-tier use currently release amounts to the environment which are very small in comparison to the amounts entering land disposal sites from these industries. However, these effluents can have severe local impacts, as evidenced by the current PCBs problem in the Hudson River.

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(5) Monsanto and portions of the electrical equipment industry utilizing PCBs have greatly reduced PCB releases to water and land over the past few years, primarily through improvement of plant housekeeping, improved waste collection and handling, and disposal of liquid wastes through incineration.

(6) There is no plant-scale process used at present for the specific purpose of removing PCBs from industrial wastewater.

(7) The best available treatment technology for removal of PCBs from wastewater is carbon adsorption coupled with solids and oil/grease removal. Carbon treatment can produce end-of-pipe PCBs concentrations of one ppb or less. Other adsorbents, such as resins, also appear effective to this extent.

(8) The most promising method, of those water treatment technologies under development, for PCBs destruction is ultraviolet-catalyzed ozonation.

(9) Incineration is an effective method of disposal for liquid PCBs. Landfilling is the only generally available disposal method for PCBs-contaminated solid wastes, but incineration of these wastes is technically feasible.

(10) "Zero discharge" to water of PCBs from production and first-tier use is available only through extensive water reuse plus extensive incineration of lightly contaminated wastewaters.

(11) Significant amounts of solid PCB (decachlorobiphenyl, or deka) wastes are stored or disposed of on land by the investment casting industry. Air emissions of deka may also be significant in amount, but no evidence of potential health hazards from this material has been reported.

(12) The total present usage of PCBs for open and semi-closed applications is not known but is believed to be small in comparison to closed electrical system usage. A few capacitor manufacturing

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plants report recent use of PCBs in vacuum pumps, and a significant amount of carbonless copy paper containing PCBs must still be in inventory and in files.

(13) Chlorination of waste biphenyl in industrial wastewaters discharged into municipal sewers is a potential mechanism for inadvertent production of PCBs.

(14) PCBs are uniquely suited to the requirements of capacitors for AC service. Although a number of potential substitutes for this application are under development and test, they are all more flammable than Aroclor 1016 and neither their performance in service nor their potential toxicity to man and other species have been evaluated sufficiently to allow a definitive comparison with 1016.

(15) Alternatives to PCBs usage in new transformers are available. In addition, testing of promising substitute fluids (termed "self-extinguishing") is underway; these fluids may gain industry-wide acceptance within three years as substitutes for PCB fluids. At present, specification of PCB-filled transformers appears to be based primarily on cost considerations.

(16) No technical barriers to substitution for PCBs (deka) in investment casting waxes are apparent. Several potential alternatives have been previously used by this industry.

(17) Atmospheric fallout is a major source of PCBs input to fresh water systems. In Lake Michigan, the PCBs contribution at present appears to be much larger than the total of PCBs inputs from point sources such as municipal sewage treatment and paper recycling.

(18) The importance of atmospheric transport of PCBs relative to other potential inputs to water indicates that the availability of environmental sinks from PCBs is limited, possibly due to short residence times to evaporation in sea water.

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(19) At present, regulatory authority over PCBs in the United States is insufficient to significantly reduce future PCBs inputs to the environment, although inputs directly to the waterways from industrial sources can be reduced from their present level. Current disposal practices, except for incineration, tend to delay instead of prevent the PCBs entry into the "free" (available to the biota) state, and these practices are regulated only minimally.

2.0 RECOMMENDATIONS

During December, 1975 and January, 1976, EPA Administrator Russell Train called for a cooperative effort between Government and industry to eventually eliminate PCBs from production and usage in the United States. The recommendations listed below were developed with this objective in mind, although each recommendation also reflects the still existing needs for further definition of the current and future PCBs problem and for the development of methods for reducing the potential damage to human health and the environment.

(1) The current distribution and losses to the environment of PCBs should be defined more accurately. Study is needed for the following aspects of past and present usage:

(a) Present extent and distribution of usage in semi-closed systems such as heat transfer and hydraulic systems (dissemination of information concerning PCBs effects and available substitutes will result in voluntary reduction of PCBs usage);

(b) Definition of past and present usage in investment casting, including quantification of air emissions, disposal on land, and waterborne contamination;

(c) Present distribution and projected future trends for PCBs in the pulp and paper industry, especially the secondary fiber recovery portion; and

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(d) Extent of inadvertent PCBs contamination in effluents from other industries which are currently not purchasers of PCBs.

(2) The basic transport properties of PCBs, particularly those relating to evaporation and atmospheric fallout, should be studied in depth. This and other information should be used to investigate global transport characteristics of PCBs and to predict the potential magnitude of the global PCBs problem. Potential sinks and destruction methods for PCBs should be investigated.

(3) The type of analysis presented herein for Lake Michigan should be further expanded and refined for application to other important fresh water systems. The model should be extended to a prediction of future effects and the influence of possible reductions in PCBs usage.

(4) Transport of PCBs from landfills should be investigated; in particular, potential methods for delaying or reducing PCBs release from landfills should be studied.

(5) Development and testing of potential substitutes for PCBs in capacitors, transformers, and investment casting waxes should be encouraged strongly. Technical and institutional barriers to the use of alternatives should be attacked on all possible fronts as soon as possible. Extensive toxicological testing of proposed substitute materials should be performed prior to acceptance.

(6) Methods for treatment of PCBs-contaminated water effluent should be developed and applied. Research and development activities on directly destructive treatment methods, such as UV-assisted ozonation and catalytic oxidation or reduction should be encouraged, but further work on adsorptive techniques is also needed.

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(7) Alternative approaches and schedules for PCBs elimination from U.S. commerce should be evaluated with regard to technical feasibility, institutional acceptability, and economic and environmental impact. Based on these considerations, an optimized path to PCBs elimination should be developed.

(8) Possible inadvertent formation of PCBs in the environment should be studied; in particular, it is recommended that the chlorination of biphenyl in wastewaters be evaluated as a potential source of PCBs.

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SECTION IV

CHEMICAL AND PHYSICAL PROPERTIES OF CHLORINATED BIPHENYLS

1.0 INTRODUCTION

The purpose of this section is to present a précis of the salient characteristics of the commercial preparations of the polychlorinated biphenyls which have generated concern as environmental pollutants. The emphasis is directed to those properties that have led to the relatively widespread use of these materials. In addition, attention will also be directed to those physical and chemical properties that contribute to the environmental effects arising from the general distribution of these materials. The discussion is not meant to be exhaustive, but rather to offer the basic technical information that is used to support the other sections of the total report. The most complete compilation of the relevant information that has been published to date is that by Hutzinger et al (O. Hutzinger, S. Safe, and V. Zitko, "The Chemistry of PCBs", CRC Press, 1974) and the authors express their debt to this publication.

1.1 The Chemistry of the Chlorinated Biphenyls

The polychlorinated biphenyls (PCBs) constitute a large class of compounds produced by the partial (or complete) chlorination of the biphenyl molecule. Since their introduction in 1929 in commercial quantities, these compounds, or rather commercial mixtures of various members of the class, have been applied in a considerable variety of industrial applications. The unique physical and chemical properties of these compounds, including low vapor pressure at ambient temperatures; resistance to combustion; remarkable chemical stability; high dielectric constant and high specific electrical resistivity have been utilized in such applications as electrical insulating fluids; fire resistant heat transfer and hydraulic fluids; lubricants for use at high temperatures and pressures in critical applications and as a constituent in a variety of elastomers, adhesives, paints, lacquers, varnishes, pigments and waxes.

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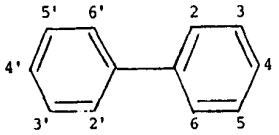
PCBs and mixtures of chlorobiphenyls have been produced in a number of countries and marketed under several trade names including Aroclor, Clophen, Phenoclor, Kanechlor and Fenclor. The essential characteristics of all these mixtures, which depend in detail on the specific mixtures of chlorobiphenyls that make up the specific preparation, are sufficiently alike that it will suffice to discuss all in terms of the Aroclors, which is the trade name of the preparations of Monsanto Chemical Company. In those special cases wherein there is some particular property peculiar to one of the foreign PCB mixtures, a note will be made.

A great deal of confusion has appeared in the literature because of the nomenclature that is used to describe the commercial preparations and the individual authenticated chlorobiphenyls. In order to clarify the nomenclature to be used herein, it is appropriate to digress briefly as follows. The biphenyl molecule has a total of ten (10) carbon-hydrogen bonds at which chlorine substitution can be accommodated. A schematic representation of the biphenyl molecule with the various positions at which substitution can be accomplished numbered in the American Chemical Society standard notation is presented below:



ACS Convention for Numerical Assignments
of Biphenyl Substitution

In the interest of a common usage, the following rules will be followed in this report:

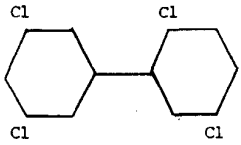
a. When referring to a mixture of different species, as occurs in the commercial products, we will use the term polychlorinated biphenyls or the acronym PCB.

b. Those species of chlorinated compounds that arise from a specified number of chlorine substituents on the biphenyl molecule will be referred to as chlorobiphenyls with a suitable numerical prefix to define the number of substituted chlorines; i.e., dichlorobiphenyl. Thus, there are a total of ten (10) chlorobiphenyls that might appear in the commerical mixtures.

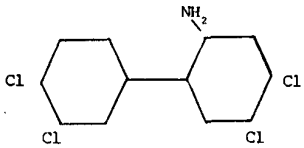
c. Those specific compounds that represent the class of compounds formed by a specific number of substituent chlorine atoms but differ in the locations at which substitution has taken place are referred to as isomers.

Thus, in terms of the above, the proper manner of referring to a commercial PCB mixture is as a "mixture of chlorobiphenyls containing various proportions of the isomers of each".

To illustrate the utility of the numbering system indicated previously, the correct names of the compounds shown below are:



2,3',5,5'-tetrachlorobiphenyl



3',4,4',5-tetrachloro-2-biphenylamine

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The ten chlorobiphenyls and some of the salient chemical data are listed in Table 1.1-1; note that the total of all the isomers of the chlorobiphenyls are 209 separate compounds.

1.2 Commercial Production and Chemical Makeup of the Aroclors

The commercial process by which the PCBs are made involves the chlorination of biphenyl with anhydrous chlorine in the presence of a catalyst which may be either iron filings or ferric chloride. The crude product is generally purified to remove color, traces of hydrogen chloride, and the catalyst by treatment with alkali and subsequent distillation. The resulting product is then a more or less complex mixture of the chlorobiphenyls, the precise composition depending on the conditions under which chlorination was carried out. The approximate composition of selected Aroclors is given in Table 1.2-1.

By way of explanation, the products made by Monsanto under the tradename Aroclor are designated as to the starting material, with biphenyl represented by the 12 prefix, and with the approximate chlorine percentage by the second set of digits; i.e., Aroclor 1248 is a chlorinated biphenyl containing approximately 48 percent chlorine.

From the data presented in Table 1.1-1 and 1.2-1, it might be inferred that all of the isomers of the individual chlorobiphenyls are to be found in each of the commercial mixtures. To illustrate the actual situation, Aroclor 1248, which is made up primarily of the di-, tri-, tetra-, penta- and hexa- chlorobiphenyls, could be expected to contain something of the order of 140-150 separate isomers. In point of fact, there are less than 50 identifiable peaks observed in the high resolution gas chromatogram of typical specimens of Aroclor 1248 as is illustrated in Table 1.2-2.

The observations relative to the high resolution studies of the commercial Aroclor mixtures have been summarized by Hutzinger, et al (ibid), in the form of Figure 1.2-1 which indicates the structural units of which the significant isomers are constructed.

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Table 1.1-1
Empirical Formulation, Molecular Weights
and Chlorine Percentage in PCBs

Empirical formula chlorobiphenyls	Molecular weight*	Percent chlorine*	No. of isomers
$C_{12}H_{10}$	154	0	1
$C_{12}H_9Cl$	188	18.6	3
$C_{12}H_8Cl_2$	222	31.5	12
$C_{12}H_7Cl_3$	256	41.0	24
$C_{12}H_6Cl_4$	290	48.3	42
$C_{12}H_5Cl_5$	324	54.0	46
$C_{12}H_4Cl_6$	358	58.7	42
$C_{12}H_3Cl_7$	392	62.5	24
$C_{12}H_2Cl_8$	426	65.7	12
$C_{12}HCl_9$	460	68.5	3
$C_{12}Cl_{10}$	494	79.9	1

*Based on Cl^{35}

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Table 1.2-1

Approximate Molecular Composition
of Selected Aroclors

Chlorobiphenyl	Aroclor Type or Grade (percent composition)					
	1221	1242	1248	1254	1260	1016
$C_{12}H_{10}$	11	<0.1		<0.1		<0.1
$C_{12}H_9Cl$	51	1		<0.1		1
$C_{12}H_8Cl_2$	32	16	2	0.5		20
$C_{12}H_7Cl_3$	4	49	18	1		57
$C_{12}H_6Cl_4$	2	25	40	21		21
$C_{12}H_5Cl_5$	0.5	8	36	48	12	1
$C_{12}H_4Cl_6$	ND	1	4	23	38	<0.1
$C_{12}H_3Cl_7$	ND	<0.1		6	41	ND
$C_{12}H_2Cl_8$	ND	ND		ND	8	ND
$C_{12}H_1Cl_9$	ND	ND		ND	1	ND
$C_{12}Cl_{10}$	ND	ND		ND		ND

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Table 1.2-2

High Resolution Gas Chromatography of Aroclor 1248

Peak number*	No. of Cl	% In Aroclor 1248	% In fatty tissue
1			
2			
3			
4	2	0.4	
5	3	1.0	0.9
6	2	3.2	1.4
7	3	11.2	0.9
8	3	3.2	2.4
9	3	3.1	0.5
10	3	2.0	0.2
11/12	3,4	1.4	4.8
13	3,4	1.4	0.8
14	3,4	0.8	0
15	3	8.5	1.6
16	3	9.7	1.6
17	3	2.1	0.8
18	3,4	7.4	0.5
19	3,4	7.4	-
20	3,4	6.0	7.0
21	3,4	4.5	4.1
22	4	3.1	0.3
23	4	2.6	0.4
24	3,4,5	0.8	-
25	4,5	1.2	1.0
26	4,5	1.0	-
27	4	0.2	-
28	4	5.0	5.3
29	4	3.3	2.0
30	4	2.0	0.4
31	4	2.1	0.5
32	4,5	1.0	2.9
33	4,5	0.5	29.0
34	4,5	0.5	1.4
35	4,5	0.8	-
36	5	1.0	1.7
37	5	0.4	1.4
38	6	<0.1	0.1
39	4	<0.1	0.1
40	6	0.2	11.0
41/42	5	0.3	1.1
43	5,6	0.2	8.0
44	6	<0.1	5.3
45	6	0.2	0.9
46	6,7	(0.7)	(1.1)

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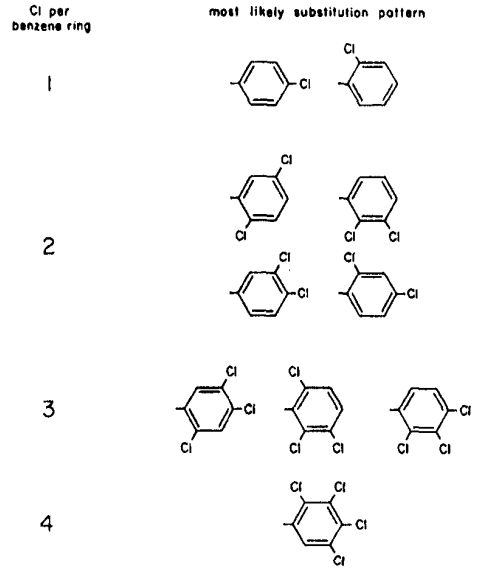
Figure 1.2-1

Moieties from Which Principal
Chlorobiphenyl Isomers are Formed



The most common substitution patterns for the chlorobiphenyls found in PCB preparations. Only one phenyl-ring is shown. The most abundant tetrachlorobiphenyls, for example, are those from the dichlorophenyl-moieties shown. One di- and one trichlorophenyl- would give most abundant penta-chlorobiphenyls, etc.

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Several comments are necessary at this point: The importance of such detailed determination and identification of the isomers characteristic of the commercial PCBs lies in the observations, to be discussed below, that bio-accumulated chlorobiphenyls show what appear to be significant differences in the distributions of the individual isomers from the source materials. The most probable explanation for these observations seem to be that at least some of the chlorobiphenyls are metabolized principally to hydro-chlorobiphenyls. Only after very complete isomeric spectra are available can such effects be properly studied.

Secondly, the detailed study of the PCBs has shown that there are no major compounds in these mixtures aside from the chlorobiphenyls. On the other hand, products formed by the addition (rather than by substitution) of chlorine to the biphenyl molecule in laboratory studies, yield significant concentrations of partially saturated structures. These structures are apparently either not formed under the conditions of chlorination that prevail during the industrial processing or alternatively are destroyed during the purification steps of the process. In contrast to the Aroclors, some of the foreign products have shown traces of polychlorinated naphthalenes and polychlorodibenzofurans; a fact that may have considerable toxicological significance in view of the rather more toxic nature of these latter products. However, recent information published by FDA indicates that impurities of chlorodibenzofurans have been also detected in Aroclors.

1.3 Physical Properties of the PCB Aroclors

The relevant physical properties of the Aroclor mixtures naturally separate into two groups; those properties that have led to the widespread industrial use of these materials, and those properties that result in the introduction of these materials into the environment with what appears to be considerable potential danger.

1.3.1 Physical Properties of Industrial and Technical Interest

The most useful compilation of the physical properties of the various Aroclors that has so far appeared in the literature is that given by Hutzinger, et al (ibid), a portion of which is herein reproduced (with minor changes) as Table 1.3.1-1.

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nm = not reported
* = some chlorine content no data chlorobiphenyl
** = polychlorinated terphenyls

Table 1.3.1-1

Chemical and Physical Properties of Representative Aroclors

Property	Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268	Aroclor 1270*	Aroclor 5442	Aroclor 5460**
Appearance	Clear, mobile oil	Clear, mobile oil	Clear, mobile oil	Clear, mobile oil	Clear, mobile oil	Light-yellow viscous liquid	Light-yellow soft, sticky resin	Light-yellow sticky viscous resin	White to off-white powder	White crystalline powder	Yellow, transparent sticky resin	Clear yellow-ochre brittle resin
Odor, maximum	100 APHA	100 APHA		100 APHA	100 APHA	100 APHA	150 APHA	150 APHA	1.5 Pfa (solids)			
Chlorine, percent	20.5-21.5	31.4-32.5	~41	42	48	54	60	61.5-62.5	68	71	42	60
Acidity, mg KOH/g maximum	0.014	0.014		0.025	0.020	0.010	0.014	0.014	0.05			
Moisture, ppm, maximum	-	-		50	50	50	50	-	-			
Ave. coefficient of expansion, cc/cc/°C	0.00871 (15°-40°C)	0.00873 (25°-100°C)		0.00066 (25°-65°C)	0.00070 (25°-65°C)	0.00066 (25°-65°C)	0.00067 (25°-100°C)	0.00064 (25°-65°C)	0.00067 (25°-100°C)			
Specific gravity	1.180-1.182 (25°/15.5°C)	1.378-1.388 (25°/15.5°C)	1.382-1.392 (25°/15.5°C)	1.381-1.392 (25°/15.5°C)	1.405-1.425 (61°/15.5°C)	1.495-1.505 (61°/15.5°C)	1.555-1.566 (98°/15.5°C)	1.572-1.583 (98°/15.5°C)	1.804-1.811 (25°/25°C)	1.916-1.960 (25°/25°C)	1.478 (25°/25°)	1.670 (25°/25°C)
Density, lb/gal.25°C	9.85	10.55	11.49	11.59	12.04	12.82	13.58	13.72	15.09	16.30	12.25	13.90
Distillation range, °C, corrected (ASTM D-20, modified)	275-320	290-375	323-356	325-366	340-375	365-390	385-420	390-425	435-450	450-468	215-300	280-375
Evaporation loss, 5, 150°C, 6 hr (ASTM D-6, mod.) 165°C, 5 hr	1.0-1.5	1.0-1.5		0-0.6 3.0-3.6	0-0.2 3.0-4.0	0-0.2 1.1-1.3	0-0.1 0.5-0.8	0-0.1 0.5-0.6	0-0.06 0.1-0.2			
Flash point °C (Cleveland Open °F Cup)	141-154 286-302	153-154 305-310	170	176-188 340-356	193-196 379-384	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none	247	none
Fire point °C (Cleveland Open °F) Cup)	176 349	238 460	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none	>358	none
Pour point °C (ASTM D-97) °F	1 (normaldol) 34 (ethylene)	-28.5 -38		-19 2	-7 19.4	10 50	21 69	35-38 99	- -		46	—
Softening point °C (ASTM E-28) °F	-	-		-	-	-	-	-	140-170 302-338 (Ball point)	249-300	66-82	98-105.5
Refractive index, n 0-20 20°C	1.617-1.619	1.620-1.622	1.622-1.624 @ 25°C	1.623-1.629	1.630-1.638	1.629-1.641	1.647-1.649	1.6501-1.6517	-			1.660-1.665
Viscosity, SUS Saybolt Universal (ASTM D-88): 100°F (37.8°C) 130°F (54.5°C) 210°F (98.9°C)	32-41 29-32 29-31	49-51 39-41 31-32	31-40 nm nm	42-52 40-56 34-35	85-140 73-80 36-37	1000-2500 250-340 44-48	4200-4500 72-78	600-650 (160°F/ 71°C) 86-100	-			
Average no. of Cl/mol	2.15	2.84	nm	3.38	3.30	4.96	6.30	6.80	8.76	NR	NR	NR

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In addition to the chemical stability and resistance to combustion illustrated in Table 1.3.1-1, the electrical properties of the PCB Aroclors are of extreme significance in the utilization of these materials. A compilation of the relevant data is presented as Table 1.3.1-2, which illustrates the nature of the problem that is encountered when one undertakes a search for a suitable substitute for these compounds in such segments of the electrical industry as the manufacture of capacitors. Specifically, the dielectric constants for most dielectric liquids lie in the range up to perhaps half of that of the polychlorinated biphenyls.

1.3.2 Physical Properties of Environmental Interest

The essentially world-wide distribution of the chlorinated hydrocarbons such as the PCBs suggest that a major route by which such compounds are transported is through the atmosphere either in the form of vapor or perhaps sorbed onto dust particles. In addition, it is observed that there is a widespread accumulation of these compounds within the biota ranging from the smallest on up the food chain until truly enormous loads are found in the highest members of the chain. Since this bioaccumulation also includes the aquatic biota, the possibility of considerable transport via the solubility of these compounds in water must also be taken into account. Table 1.3.2-1 lists some of the vapor pressure and solubility data for several of the Aroclors (D. MacKay and A. W. Wolkoff, Env. Sci. and Tech., 7, 611 ff (1973)).

The analysis of co-evaporation (MacKay, ibid) of dilute solutions of the Aroclors by equilibrium thermodynamics suggests that, because of the very high activity coefficients of the chlorobiphenyls in water, the potential for evaporation is quite high enough that this mechanism is a major portal by which such compounds enter the atmosphere. The fourth column of Table 1.3.2-1 indicates the theoretical time for a fifty percent reduction in the concentration of the Aroclor from a saturated water solution (pure water plus PCBs), assuming the water depth to be 1 meter thick. Clearly, the results of this analysis need to be experimentally verified.

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Table 1-3.1-2
Electrical Properties of Some Aroclors

Aroclor	Dielectric constant at 1000 cycles[a] 25°C	100°C	Volume resistivity,[b] 8 cm at 100°C 500 V, de	Dielectric strength,[c] kV	Power factor,[a] 100°C, 1000 cycles, %
1232	5.7	4.6			
1242	5.8	4.9	above 500 x 10^9	>35	<0.1
1248	5.6	4.6	above 500 x 10^9	>35	<0.1
1254	5.0	4.3	above 500 x 10^9	>35	<0.1
1260	4.3	3.7	above 500 x 10^9	>35	<0.1
1268	2.5				
5442*	3.0	4.9	above 500 x 10^9	--	--
5460*	2.5	3.7	---	--	--

[a]ASTM D-150-47T

[b]ASTM D-257-46

[c]ASTM D-149-44

*Polychlorinated terphenyls

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Table 1.3.2-1

Solubility, Vapor Presure and Halflife for
Vaporization from Water of Selected Aroclors at 25°C

PCB Type	Solubility (mg/l)	Vapor Pressure (mm Hg)	Theoretical halflife for vaporization from 1 m. water column
Aroclor 1242	0.24	4.06×10^{-4}	5.96 hr.
Aroclor 1248	5.4×10^{-2}	4.94×10^{-4}	58.3 min.
Aroclor 1254	1.2×10^{-2}	7.71×10^{-5}	1.2 min.
Aroclor 1260	2.7×10^{-3}	4.05×10^{-5}	28.8 min.

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As pointed out above, not only is each of the Aroclors a mixture of several chlorobiphenyls, but there are a number of isomers present for each of the chlorobiphenyls. Thus, the solubility of an Aroclor, or the vapor pressure of an Aroclor, represents an average over the various species that make up the mixture. To illustrate the effect of the structural complexity, Table 1.3.2-2 (Hutzinger, ibid) details the measured vaporization rates of the several Aroclors. On the other hand, the changes in the mixture corresponding to Aroclor 1254 on extended heating are displayed in Table 1.3.2-3 (Hutzinger, ibid).

The possible implications of these data lie in the fact that much of the Aroclor that is found in typical environmental samples seems to demonstrate lesser amounts of the lower chlorine number chlorobiphenyls than is characteristic of freshly manufactured samples. This observation has frequently been attributed to possible metabolism of the more lightly chlorinated species coupled with enhanced fixation of the higher chlorinated species.

A partial listing of the measured solubility in water of identified authentic chlorobiphenyls is shown in Table 1.3.2-4 (Hutzinger, ibid) and the effect of the solubility differences of the individual chlorobiphenyls on the constitution of Aroclor 1254 solutions is illustrated in Table 1.3.2-5 (Hutzinger, ibid).

A factor that is most probably of considerable importance in the admission of such compounds as the PCBs into the environment is a measure of the partition coefficients between such interface systems as soil-air; soil-water; lipids-water; and, more generally, water-solid particles. At the present time there seems to be very little actual data available in direct form, although much should be possible to infer from the effects of various combinations of stationary phase and support in gas chromatography on the retention index. An interesting and probably significant point of datum has been presented by D. R. Branson of the Dow Chemical Co., who reports that the distribution of 2,2',5 trichlorobiphenyl between sludge-water-air was 92%-3%-5%, respectively.

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Table 1.3.2-2

Vaporization Rates of Aroclors

Aroclor (Surface area: 12.28 cm^2)	Wt. loss (g)	Exposure at 100°C (hr)	Vaporization rate ($g/cm^2/hr$)
1221	0.5125	24	0.00174
1232	0.2572	24	0.000874
1242	0.0995	24	0.000338
1248	0.0448	24	0.000152
1254	0.0156	24	0.000053
1262	0.0039	24	0.000013
1260	0.0026	24	0.000009
1270 (Deca)	0.0015	24	0.000005

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Table 1.3.2-3

Percent Loss in Area of Seven Chromatogram Peaks of Aroclor After Heating

Aroclor 1254 peak	% Peak Remaining After Heating with water 25 min	with water 60 min	without water 10 min
1	34	17	13
2	59	26	15
3	78	27	20
4	60	46	20
5	86	49	27
6	100	85	28
7	100	67	16

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Table 1.3.2-4

Solubility of Chlorobiphenyls in Water

Compound	Solubility mg/l (ppm)
Monochlorobiphenyls	
2-	5.9
3-	3.5
4-	1.19
Dichlorobiphenyls	
2,4-	1.40
2,2'-	1.50
2,4'-	1.88
4,4'-	0.08
Trichlorobiphenyls	
2,4,4'-	0.085
2',3,4-	0.078
Tetrachlorobiphenyls	
2,2',5,5'-	0.046
2,2',3,3'-	0.034
2,2',3,5'-	0.170
2,2',4,4'-	0.068
2,3',4,4'-	0.058
2,3',4',5-	0.041
3,3',4,4'-	0.175
Pentachlorobiphenyls	
2,2',3,4,5'-	0.022
2,2',4,5,5'-	0.031
Hexachlorobiphenyl	
2,2',4,4',5,5'-	0.0088
Octachlorobiphenyl	
2,2',3,3',4,4',5,5'-	0.0070
Decachlorobiphenyl	0.015
4,4'-Dichlorobiphenyl	
+Tween 80 0.1%	5.9
+Tween 80 1%	>10.0
+Humic acid extract	0.07

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Table 1.3.2-5

Relative Peak Heights (Peak 5 = 100) in Saturated Aqueous Solutions of Aroclor 1254

Peak No.	Saturated aqueous solution (26°C)	Saturated aqueous solution (4°C)	Aroclor 1254 standard
1	172	144	35
2	91	72	16
3	47	41	30
4	14	9	1
5	100	100	100
6	33	28	23
7	57	59	55
8	5	5	10
9	21	24	25
10	8	13	31
11	4	4	6
12	11	24	50
13	6	10	11

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1.4 Chemical Properties of the Chlorobiphenyls

Considerable detail on the most important chemical reactions that are known to occur with the chlorobiphenyls is presented in Chapter 5 of the treatise on "The Chemistry of the PCB" by Hutzinger, et al. Suffice it to say here that oxidation and hydrolysis can be carried out, but only under conditions which are considerably more rigorous than would be obtained in industrial applications. This relative stability is, of course, one of the most attractive features of these compounds in technological practice.

The class of reactions to which the chlorobiphenyls are susceptible and which is of most interest in terms of their possible toxicological significance are those which result in cyclization. Of particular interest in this context is 2,2' dichlorobiphenyl, which on cyclization yields the compound dichlorodibenzofuran. The toxicological data on these two compounds indicates the nature of this change: the LD_o for oral doses to rats is of the order of 250 mg/kg for the dibenzofuran whereas the corresponding toxicity for the chlorobiphenyl is in excess of 4000 mg/kg. (Data from the "Toxic Substances List", HEW, 1973).

The close proximity of the 2 and 2' substituents on the biphenyl molecule facilitates intermolecular cyclization reactions under a variety of conditions. Of special interest is the observation that alkali fusion of 2-chloro-2'-hydroxybiphenyl and the dehydration of 2,2'-dihydroxychlorobiphenyl yield the corresponding chlorodibenzofurans; hydroxylation of the chlorobiphenyls is the common initial step in the metabolism of these compounds. The immediate biological significance of this is unknown at this time since the chlorodibenzofurans have not been isolated from animal experiments.

1.5 Photochemical Reactions Involving the PCBs

A great deal of effort has been directed to the study of the effects of ultraviolet (UV) radiation on the chlorobiphenyls since photodestruction is believed to be a possible major mechanism for the environmental decay of chlorohydrocarbon pesticides such as DDT. There has been much speculation as to the role that UV photodisintegration might play in terms of the chlorinated biphenyls. The earlier work was carried out using mercury vapor UV sources with the result

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that, because of the significantly harder radiation (mercury source 250 nm, solar radiation at surface of the earth with an effective cutoff at 290 nm), cross section and reaction paths are difficult to extrapolate to environmental situations. In more recent times, such irradiation studies have been carried out using General Electric "Black Light" sources which much more nearly approximate the spectral distribution of solar radiation.

A number of types of effects have been observed including partial dechlorination and even, in some cases, the formation of very viscous semi-solids that apparently arise from complex polymerizations. Again, the extension of the experimental results to environmental conditions is somewhat limited in value since the majority of the irradiation studies have been carried out in solvents other than water. The very low solubility of even the least chlorinated chlorobiphenyls in water makes the experimental study of aqueous solutions especially difficult, particularly when the information of concern is the quantitative evaluation of the reaction products that are formed. It must be said, at this time, that the probability of UV disassociation being a major source for the environmental decay of the chlorobiphenyls seems to be significantly less than that for the chlorinated hydrocarbon pesticides.

Since it is assumed that a major portion of the chlorinated biphenyls are transported and distributed throughout the world through the medium of adsorption on dust particles or as a vapor, it follows that studies of the stability of thin sorbed films or of vapors of the chlorinated biphenyls against long term UV irradiation are of importance. The earlier attempts to discover the presence of reaction products resulting from long term exposure of selected chlorobiphenyls to solar radiation were subject to the differential evaporation of the less chlorinated species; this result seriously biased the observations. The recent experiments that have been conducted within quartz containers seem to obviate evaporation problems and, further, seem to indicate that the mono- and dichlorobiphenyls are essentially completely destroyed when exposed to hard UV for times of the order of weeks or months. Problems of detection sensitivity continue to plague attempts to elucidate the detailed mechanisms and pathways.

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Studies of thin films of chlorobiphenyls sorbed onto appropriate surfaces have also been carried out within a quartz enclosure. To date, the major objection to such experiments, in terms of extrapolation to environmental conditions, seems to be that the concentration, or rather the absolute density of the surface layer, is sufficiently high that the activated species remain in contact for sufficiently long times as to allow the formation of products that might well be very rare events in corresponding environmental concentrations.

At this time there appears to be significant research being directed to the determination of the stability of chlorobiphenyls against ultraviolet radiation and that it is to be expected that the situation which obtains in typical environmental conditions will be greatly illuminated in the near future.

1.6 Metabolic Chemistry of the Chlorobiphenyls

The very combination of physical and chemical properties that have made the chlorobiphenyls and their technical mixtures of such wide technical interest also result in these compounds being of significance as environmental pollutants, especially in terms of their impact on the biota. The very low chemical activity, coupled with high lipid-water partition coefficients, apparently contribute to the bioaccumulation whereby the chlorobiphenyls, pecially the more highly chlorinated species, tend to become fixed within the body fats and particularly in higher members of the food chain. There is evidence that this fixed load of refractory chlorinated organic materials, or the circulating levels of the same compounds that must accompany such fixed loads, represents a serious hazard to the bearer or progeny. The toxic consequences of body burdens of chlorobiphenyls is more fully discussed in the section of this report concerned with toxicology of the chlorobiphenyls.

The mechanisms by which an organism can deal with ingested refractory compounds are naturally separated into physical and chemical processes. The physical processes are primarily associated with the requirements of free energy across the boundary between differing phases such as a water-lipid boundary, or a cell wall, etc. Since there does not exist a significant body of partition coefficient data for various combinations of interfaces, little of a quantitative nature can be stated as to the biological significance of such physical processes.

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On the other hand, as is pointed out in Section 2.4, hydroxylation is a rather easily accomplished process for at least the less chlorinated chlorobiphenyls. Thus, it might be assumed that one should observe the hydroxylated chlorobiphenyls as intermediate metabolic products in a variety of organisms. Experimental data is available to indicate that such hydroxylation processes are indeed exhibited by a wide variety of organisms. The principle species related differences seem to be in the rate at which such processes are found to occur — very rapidly in rodents and very slowly in fish. In addition, once the target chlorobiphenyl has been hydroxylated to a more or less degree, there appear to be available a wide variety of species-specific addition processes which could make use of the hydroxylated molecule. Interestingly, there is to date no evidence of biologically or metabolically induced cyclization; it thus appears likely that the chlorodibenzofurans are not biologically formed.

The salient observations to date on the metabolism of chlorobiphenyls might best be summarized as follows:

a. When the challenge to the animal is a technical mixture of chlorobiphenyls, there is a preferential storage of the more highly chlorinated species, with the result that the homologue spectrum of stored PCBs often represents a more heavily chlorinated mixture than the original test mixture.

b. There is conflicting and often species-dependent data as to the mechanism by which the less chlorinated species are differentiated; whether the processes involve metabolism, physical partitioning, or some combination of such processes has not been settled.

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c. Conflicting and confusing evidence exists indicating marked differences in accumulation and differentiation between specific isomers especially at the middle levels of chlorination. These differences also seem to be species-dependent in a number of cases.

d. There is significant evidence that PCB metabolism proceeds through an intermediate step of hydroxylation (often this appears to be the terminal step whereby the increased aqueous solubility of the hydroxylated species accomplishes the end of its removal).

e. There are several observations indicating that isomerization can be accomplished during metabolic reactions. In this context, the results of Bagley and Cromartie (Bagley, G.E. and E. Cromartie, J. Chrom. 75, 219-226, (1973)), with the elimination of Aroclor 1254 in the Bobwhite, are most pertinent.

In conclusion, there has been much work directed to the study of the mechanisms whereby living organisms are able to eliminate chlorinated biphenyls from their system. In spite of this effort and because of the inherent complexity of this subject, the nature of these mechanisms remains a mystery.

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SECTION V

INDUSTRIAL CHARACTERIZATIONS

1.0 INTRODUCTION

This section discusses polychlorinated biphenyls (PCBs) production and each PCBs user (capacitor, transformer, investment casting, paper recycling and miscellaneous) manufacturing process. When known, for each operation the following information is given:

- Name and the location of companies in each category;
- A description of the processes at the facilities studied and pertinent flow diagrams, where appropriate;
- Raw waste load data per ton of PCB used and sources of these wastes;
- Water usage data in terms of gallons per day;
- Treatment and housekeeping measures practiced at the facilities and on-going PCB containment programs;
- Plant waste effluents found and their composition.

2.0 MANUFACTURING PROCESS - POLYCHLORINATED BIPHENYLS (PCBs)

2.1 Process Description

Monsanto, the sole domestic manufacturer of PCBs, manufactures this chemical in their Sauget, Illinois plant. The basic raw material is biphenyl which is manufactured from pure benzene in another Monsanto plant. The PCB manufacturing operation is conducted in two steps. First, biphenyl is chlorinated with anhydrous chlorine in the presence of ferric chloride to produce crude PCBs and then the crude PCBs are distilled to obtain the finished product. A schematic flow diagram of this process is given in Figure 2.1-1A and B.

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FIGURE 2.1-1A. PREPARATION OF CRUDE CHLORINATED BIPHENYLS-MONSANTO KRUMMRICH PLANT

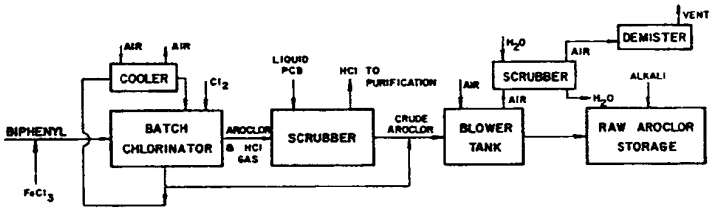
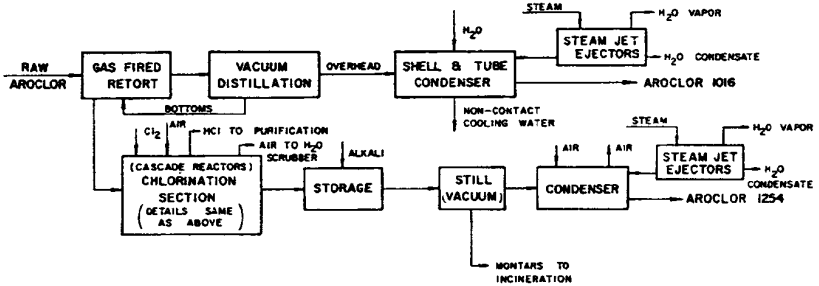


FIGURE 2.1-1B. DISTILLATION OF CRUDE PRODUCTS-MONSANTO KRUMMRICH PLANT



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The reaction section consists of 6 reactors (3 batch and 3 cascade). Currently, Monsanto manufactures four different types of Aroclors (1242, 1016, 1254 and 1221). For the manufacture of any given product, the chlorinator is charged with proper quantities of biphenyl and catalyst and heated above the melting point of biphenyl. The flow of vaporized chlorine is then started and the charge is circulated with a pump. Throughout the chlorination, the temperature is kept above the melting point of the mixture, but below 150°C to avoid excessive sublimation and plugging of the line discharging the hydrogen chlorine produced by the chlorination. The reaction pressure is maintained near atmospheric. The degree of chlorination is principally determined by the time of contact with anhydrous chlorine. The contact time varies from 12 to 36 hours for the manufacture of different Aroclor types. The degree of chlorination is measured by the specific gravity of the mixture or the ball and ring softening point when the product is viscous.

The vapors from the chlorinator (HCl containing PCBs) are scrubbed with liquid Aroclor and the gaseous HCl is sent to another plant at the Sauget complex for purification. The crude product is held at an elevated temperature and blown with dry air for several hours, after which it is sent to the raw Aroclor storage tank where a few tenths of 1 percent of alkali are stirred with the material to react with any remaining hydrogen chloride or ferric chloride. The air from the blower tank is scrubbed with water and vented to the atmosphere through a demister.

The raw Aroclor is subsequently batch distilled under reduced pressure to remove the color, and the traces of hydrogen chloride and ferric chloride. The methods of purification are different for the different types of end products. Raw Aroclor 1254, 1242 and 1221, each are distilled in stills under reduced pressure, achieved via steam jet ejectors; the condensate from the still is the finished product while the bottoms are the Montars which are drummed and sent to incineration.

The distillation section for the 1016 product consists of a gas fired retort and a vacuum distillation tower. The latter is used to allow the separation of the higher chlorinated, less biodegradable compounds from the relatively

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lower chlorinated and more biodegradable ones. The raw Aroclor (42% chlorinated material) is fed into the reboiler. The vacuum in the tower is maintained at about 100 mm Hg by steam jet ejectors. The steam is partially condensed and the condensate is discharged into the plant discharge sump. The first cut from this tower is recycled back to the retort. At a preset overhead temperature the 1016 product is collected and sent to the product storage. The high boiling residue from the tower is sent to a subsequent chlorination cycle and the resulting raw Aroclor is distilled in a still. The overhead from this still is the finished product. The bottoms from this tower are the Montars. The spent ferric chloride catalyst, used in PCB manufacturing, is sent to incineration with Montar residues.

For special orders, in order to increase electrical resistivity, the Aroclors are stirred at an elevated temperature with a few tenths of 1% of well-dried fuller's earth and then filtered through paper.

All Aroclors are stored at 150°F. Steam coils are used on the storage tanks for heating these tanks.

2.2 Raw Wastes

The raw wastes from the manufacturing area consist of the liquor from the scrubber, the condensate from the steam jet ejectors, water used for showers and eye baths, miscellaneous floor wash downs, waste oil collected in drip pans and drums, and montars which are the bottom cut from their stills. The composition and the quantities of the individual waste stream are not monitored. All effluent streams generated in the manufacturing area are directed into the sumps in this area. The waste oil collected in the drip pans and the Montars are emptied into 55 gallon drums and sent to incineration.

The raw wastes generated in the incinerator consist of the venturi scrubber liquor and the water phase from the separator sump in the incinerator area. The composition of the combined stream is monitored. However, the composition of the individual streams is not known. Non-product PCB discharges are shown in Figure 2.2-1. It has been estimated that this plant generates

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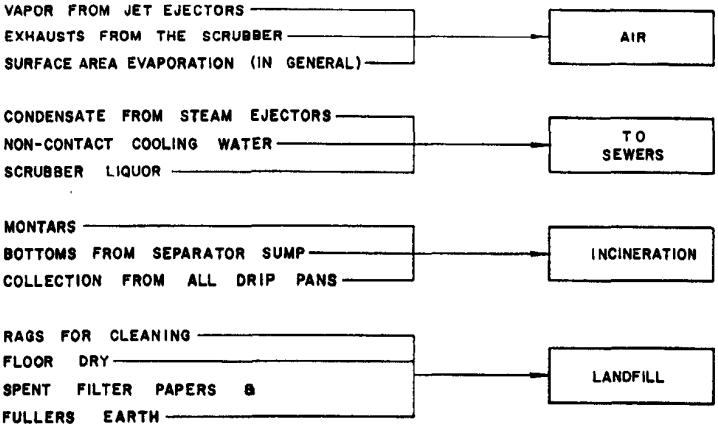
FIGURE 2.2-1. NON-PRODUCT PCB DISCHARGES AT MONSANTO'S KRUMMRICH PLANT



about 25 lbs of scrap oil and Montar per ton of PCB produced. Additionally, the quantities of material sent to landfill approximates to 5.4 lbs per ton of PCB produced. Further, Monsanto reports that the plant's PCB contribution to the air is under 1 lb/day.

2.3 Plant Water Usage

On the average, the PCB plant uses a maximum of 388,800 gallons of water and a maximum of 360,000 lbs of steam daily. Water is used for non-contact cooling purposes in shell and tube condensers, in a water scrubber, for floor washings, for showers and in eye baths. Steam is used in the steam jet ejectors and for steam tracing purposes. The plant uses municipal water and purchased steam.

The process water from this facility consists of the liquor from their scrubber and the steam condensates which are discharged in one of the two sumps in the manufacturing area.

Additionally, 273,600 gallons of water are used in the incinerator daily for quenching the hot gases from the fire box. The resulting weak muriatic acid in the quench pot is used in the venturi scrubber and in the packed tower.

The type and quantities of water used and discharged at this plant are summarized below:

Water Balance

. Manufacturing Plant

	Quantities, GPD	
	Used	Discharged
Process Water		
in water scrubber	14,400	14,400
misc. floor wash downs	7,200	7,200
condensate from steam jet ejectors	--	14,400

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Water Balance (Con't)

. Manufacturing Plant

	Quantities, GPD	
	Used	Discharged
Non contact cooling water	360,000	360,000
showers, eye bath	7,200	7,200
condensate from steam tracers	--	28,800
Total	388,800	432,000

. Incinerator

water used for hot gas quenching	273,600	273,600
water phase from the sump	--	14,400
Total	273,600	288,000

2.4 Wastewater Treatment and Housekeeping

Monsanto reports significant environmental controls at their Krummrich, Sauget plant. Since 1969, they have invested more than 22 man-years of work and millions of dollars in this program. The in-house goals have reduced the PCB discharges into water to about three pounds per day.

A John Zink designed incinerator was erected at Sauget in 1970 to safely dispose of PCBs. A schematic flow diagram of this operation is given in Figure 2.4-1. Aroclor is steam atomized and fed into the fire box. Natural gas is used for combustion and the feed is incinerated at temperature above 2200°F at 5 percent excess oxygen with a retention time of 2-3 seconds. The gases are quenched with water and the exhausts from the quench pot are passed through a high-energy venturi scrubber, then through a packed column which is irrigated by the weak muriatic acid originating from the quench pot. Exhausts are then vented to atmosphere through a demister. These exhausts as well as the effluent from the incinerator section are monitored.

In the incineration area, drainage is directed to trenches and piping which flow into a 10,000 gallon underground concrete basin. The water

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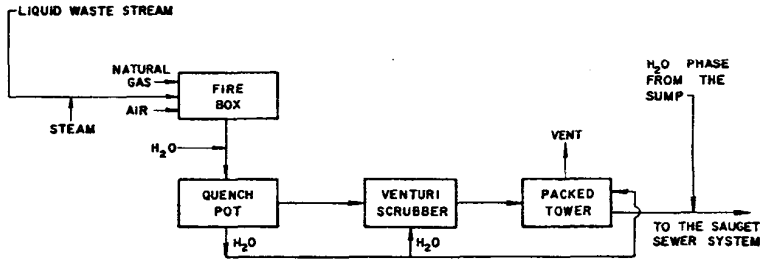
FIGURE 2.4-1. PROCESS FLOW DIAGRAM OF THE JOHN ZINK INCINERATOR AT MONSANTO'S KRUMMRICH PLANT



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layer from this basin is pumped continuously, combined with the scrubber liquor, metered, monitored and discharged into the sanitary sewers of the Sauget complex and from there it is sent to the East St. Louis municipal sewers. The organic phase from the sump is periodically pumped into waste storage tanks for incineration.

The incineration unit has a rated design capacity of 10 million pounds per year. However, since the start of its operation this unit has achieved a service factor of about 0.60. Monsanto reports that this incinerator can achieve a maximum of 6 million pounds of capacity annually; the unit is plagued with various mechanical problems.

Monsanto uses their incinerator to process both their own wastes and as a service to other industries. The service charge for incineration is an average of 5¢ per lb of material, but the cost appears to be increasing.

The incinerator feed is brought into the plant either by truck in 55 gallon sealed drums, by tank trucks or by rail. The drums are opened, picked up by a fork lift and emptied into a concrete pit. The tank truck carrying the waste liquids enters the incinerator area and the liquid waste is then pumped from the truck into the pit. The material in this pit is periodically pumped via a vertical certrifugal pump into one of the four 20,000 gallon incinerator waste feed tanks.

The rail car is brought into a designated area close to the incinerator site. The material from the rail car is normally pumped into a long term, 500,000 gallon storage tank. The material from this tank is pumped into the incinerator feed tanks located on the incinerator pad when required.

Drainage is provided along the rail tracks. These drains empty into the 10,000 gallon sump located under the incinerator pad.

In the manufacturing area, Monsanto has taken a number of significant steps to prevent loss of PCBs to the environment. Drainage is directed to trenches and piping, and then to one of two concrete 3,000-gallon underground settling basins. This insures PCB containment in case of accidental spill or

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equipment failure. Relief valve lines and atmospheric vents are routed through catch tanks, or are redirected to settling basins.

When small quantities of PCBs are collected in the settling basins of the manufacturing area they are later pumped into 55 gallon drums, and eventually incinerated. The overflow from these sumps is combined with the non-contact cooling water used at the plant, monitored and then discharged into the Sauget complex's sanitary sewer and from there to the East St. Louis municipal system.

PCBs are packed and shipped in galvanized-steel 55 gallon drums, or in railroad tank cars. All tank cars are top loaded. In the drum filling area spills are cleaned via rags or floor dry and these materials are drummed and sent to landfill located in the town of Sauget.

In the PCB truck or rail car loading area, drainage is directed into a small concrete pit. The material accumulated in this pit is periodically pumped into the basins located in the manufacturing area.

Nitrogen blanketing is provided on storage tanks to eliminate any "breathing" of the tanks and resultant PCB escape.

Mist eliminators have been installed in vapor lines to eliminate the possibility of PCBs leaving the manufacturing area through these lines.

Finally, underground sewers have been replaced with above-ground sewers, and repaired or combined with others, so that the effluent from the department can be monitored. In addition, this step will prevent any unknown buildup of PCBs in the sewer systems or any contamination of PCBs into other sewers.

A high housekeeping level is maintained in the plant itself. Housekeeping responsibilities which the operators have assumed are as follows:

. All pumps are checked for leakage on every shift. Drip pans that collect leaks are emptied into scrap PCB drums.

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- All leaks are reported and documented so that corrections can be made and settling basins observed.
- "Floor Dry" is used to absorb any PCBs that have spilled or leaked. If it becomes necessary to flush PCBs to the settling basin, a minimum amount of water is used.
- Sampling drums and scrap PCB drums are quickly palletized, labelled and transferred to the incineration area.

2.4.1 Treatment Facility for the Effluent from Sauget Complex

The processing and incineration departments' aqueous effluent enters the plant sewer system, and this system discharges into the Sauget Village waste sewer system. The combined streams then flow to the village primary treatment plant. The village treatment plant is under expansion to a secondary chemical treatment plant, scheduled for 1976 completion.

Additionally, evaluations are being conducted to include the village plant discharge in a projected regional biological treatment plant.

2.5 Plant Effluents

This plant has no point source discharge from their operation. There is a single discharge from the manufacturing operation (the combined stream of process and non-contact cooling water) to the main sewer system of the Sauget complex and there is a second discharge from the incinerator area to the same sewer system. The composition of these streams as reported by Monsanto are as follows:

	Effluent from the Manufacturing Operation	Effluent from the Incineration area
flow rate, gpd	432,000	288,000
PCBs, ppm	0.75	0.15
PCBs, lbs/day	2.70	0.36

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It has been reported that these effluents are clear liquids with essentially no suspended solids. The incinerator effluent may contain some amounts of chloride. However, no information is available on the chloride content.

3.0 PCB USER INDUSTRIES

3.1 Askarel Capacitor Manufacturing Industry

Presently 90-95 percent of all impregnated capacitors manufactured in the U.S. are of the PCB type. Two important types of capacitors are phase correctors on power lines and ballast capacitors for fluorescent lighting. Aroclor 1016 is the principal PCB used in this application; at some plants Aroclor 1242 and 1221 are also being used in limited quantities. The principal types of Aroclor impregnated capacitors and their applications are given below.

A. High Voltage Power

Generally AC capacitors are used to improve the power factor of a circuit. Power factor is the ratio of true power in watts to the apparent power as obtained by multiplying the current flowing to the load by the circuit voltage. The power factor correction can be made directly at the load or at utility substations. In the latter case high voltage units will be designed for 4,800 to 13,800 volt service. To the utility engineer the use of capacitors is purely a matter of economics. The main benefits that result from the use of capacitors are:

1. Reduction of losses associated with the delivery of electrical power to the point of use.
2. Reduction of the investment required in equipment for delivering electrical power to the point of use, which may be broken down into:
   a. Reduction of line current for the same kilowatt load.
   b. Reduction of the kva rating of equipment required to handle the same kilowatt load.

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c. Reduction of the transmission line voltage drop for a given kilowatt load.

d. Control of delivered voltage if the capacitor kva is varied.

Electric utilities also use capacitor banks in series with distribution circuits to improve voltage regulation.

B. Low Voltage Power

Capacitors installed in industrial plants at the demand site (typically large motors and welders) are designed for 230 to 575-volt service. Capacitors installed near the loads are the most efficient way to supply the magnetizing current to produce the flux necessary for the operation of inductive devices. Rates for the sale of power are generally structured to encourage power factor correction at the site, eliminating the need for the electric utility to transmit both power-producing current and magnetizing current all the way from the generator to the plant site.

The same considerations apply to induction heating applications, the principal difference being that capacitors for this application are designed for operation at 960 to 9600 Hz.

C. Lighting

Capacitors improve the efficiency of lighting systems. A fluorescent or mercury vapor lamp can be ballasted without the use of a capacitor, but the power factor of the lighting system would then be in the range of 50 to 60%. For commercial or industrial lighting with either fluorescent or high intensity discharge lamps, the use of a capacitor in the circuit provides part of the lamp ballasting and brings system power factor into the range of 90 to 95%.

D. Air Conditioning

As in the lighting applications, the capacitor improves system efficiency. Air conditioners could be made to operate without capacitors, as do home refrigerators, but because of the higher capacity required for air conditioners,

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the resultant line current would virtually eliminate home "plug-ins" and would still further overburden a seriously threatened national power network. Almost all air conditioner pump motors are of the split-winding type on which the capacitor provides phase differential for the so-called start winding, thus delivering good starting torque. The proper size capacitor permits high (90%) power factor after start-up.

E. Industrial Electronics

This market category is a catchall covering many varied applications, two important ones being motor run and power supply applications. Motor run applications are for pumps, fans, and farm feed equipment, and do not differ significantly from air conditioning applications. The power supply market uses capacitors principally to provide high power factor, but through careful design the capacitor can also provide wave shaping where desired.

3.1.1 Askarel Capacitor Manufacturing Plants

There are seventeen companies in the U.S. which manufacture askarel capacitors at nineteen plants. The name and the location of these plants are given in Table 3.1.1-1. Some plants manufacture industrial capacitors only and others manufacture power capacitors.

Ten major companies were contacted. Detailed information was obtained on six plants. Four plants were visited. The data herein represents approximately 50 percent of 1974 PCB usage in capacitor application. The PCB usage in this category was approximately 22,000,000 lbs. in 1974. The PCB usage in individual plants is considered by these companies to be confidential information. The range of PCB usage at these plants was 64,000 fold in 1974. Plant ages range from five to thirty-seven years.

Capacitors used in lighting and air conditioning applications contain 0.05 to 1.0 lbs. of Aroclor. The largest power capacitors contain about 77 lbs. of Aroclor. The most popular size contains 36 lbs. A sketch of a medium size industrial capacitor is shown in Figure 3.1.1-1. Capacitors are not rebuilt and returned to service after failure. They are disposed of and replaced by new units. G.E. reports that high voltage utility capacitors, low voltage

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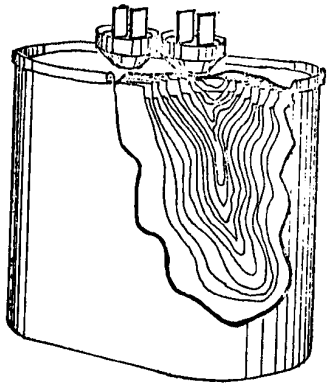

FIGURE 3.1.1-1. MEDIUM SIZE
INDUSTRIAL CAPACITOR

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Table 3.1.1-1

U.S. Capacitor Manufacturing Industry Using PCBs

Company Name (In order of PCBs Usage)	Location of the Plant
General Electric Company	Hudson Falls, N.Y. Ft. Edward, N.Y.
Westinghouse Electric Corp.	Bloomington, Ind.
Aerovox	New Bedford, Mass.
Universal Manufacturing Corp.	Bridgeport, Conn. Totowa, N.J.
Cornell Dubilier	New Bedford, Mass.
P.R. Mallory & Co., Inc.	Waynesboro, Tenn.
Sangamo Electric Co.	Pickens, S.Carolina
Sprague Electric Co.	North Adams, Mass.
Electric Utility Co.	LaSalle, Ill.
Capacitor Specialists Inc.	Escondido, Calif.
JARD Corp.	Bennington, Vt.
York Electronics	Brooklyn, N.Y.
McGraw-Edison	Greenwood, S. Carolina
RF Interonics	Bayshore, L.I., N.Y.
Axel Electronic, Inc.	Jamaica, N.Y.
Tobe Deutschmann Labs.	Canton, Mass.
Cine-Chrome Lab, Inc.	Palo Alto, Calif.

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power capacitors, and induction heating capacitors are manufactured at a rate of 200,000 per year, about 2 to 3% of which are replacements; the balance are for new installations. The current market for capacitors used in lighting applications is about 44,000,000 units annually of which 10% are estimated to be replacement ballasts. The current market for capacitors in air conditioning application is above 12,000,000 units annually, with 5% of these estimated to be for replacement usage. The market for capacitors in industrial electronics applications is estimated at 23,000,000 units per year with no estimate as to the relative size of the replacement market.

3.1.1.1 Askarel Handling

In most plants PCBs are shipped via tank car to a rail siding several miles from the plant. Individual plants provide a designated tank truck for the transfer of the PCBs from the rail yard to the manufacturing plant. To large plants, PCBs are brought via rail cars into the plant site.

In most plants PCBs are unloaded and transferred to the PCB storage tank without the benefits of any curbs or dikes. At a very few plants, the unloading operation of the PCBs from the tank car to the storage facility is confined and the receiving area is roofed and diked.

PCBs from the raw storage PCB tanks are filtered through fuller's earth and stored in finished product storage tanks. PCBs are next pumped from the storage tanks to the impregantion areas for use. Excess PCBs from these areas are recycled back to a designated tank and from there either filtered and reused or, if defective, are pumped into the scrap storage tank.

Spent fuller's earth employed at these plants is either drummed and stored at the plant site or is sent to a landfill.

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3.1.1.2 Process Description

Most plants in this category manufacture either large power capacitors or small (including less than 2 lbs. of PCBs) industrial type units. The large capacitors are either flood filled or manifold filled. All small capacitors are flood filled either in a vacuum tank or in an automatic "carousel" arrangement where loading and unloading occurs at one station, and the capacitors in each cell are progressively dried, evacuated and filled.

A generalized schematic flow diagram for the manufacture of large capacitors and small industrial capacitors are given in Figures 3.1.1.2-1 and 3.1.1.2-2, respectively. The basic manufacturing operation at these plants can be divided into two major operations.

a) Non PCB related operations consist of the following steps:

- Fabrication of capacitor cans, covers and brackets from sheet aluminum or steel. Smaller plants, however, purchase capacitor casings, capacitor terminals, connectors and foil.
- Vapor degreasing or detergent washing of metal components. At some plants, ultrasonic cleaning is used to clean smaller components.
- Roll winding the capacitor paper or polypropylene film with aluminum foil.
- Complete assembly of capacitor components and sealing the covers. In some units fill holes are provided for PCB introduction; in others PCBs are introduced through bushings or a valve.
- Leak testing via mass spectrometer and pressure testing prior to vacuum drying.

b) PCB related operations

Three completely different impregnating techniques are employed by this industry.

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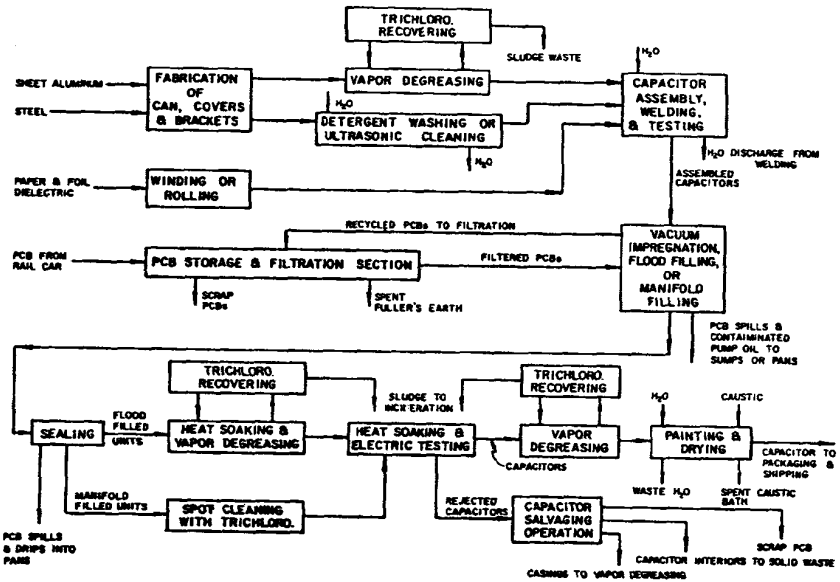

Figure 3.1.1.2-1
GENERALIZED FLOW DIAGRAM FOR THE MANUFACTURING OF LARGE CAPACITORS

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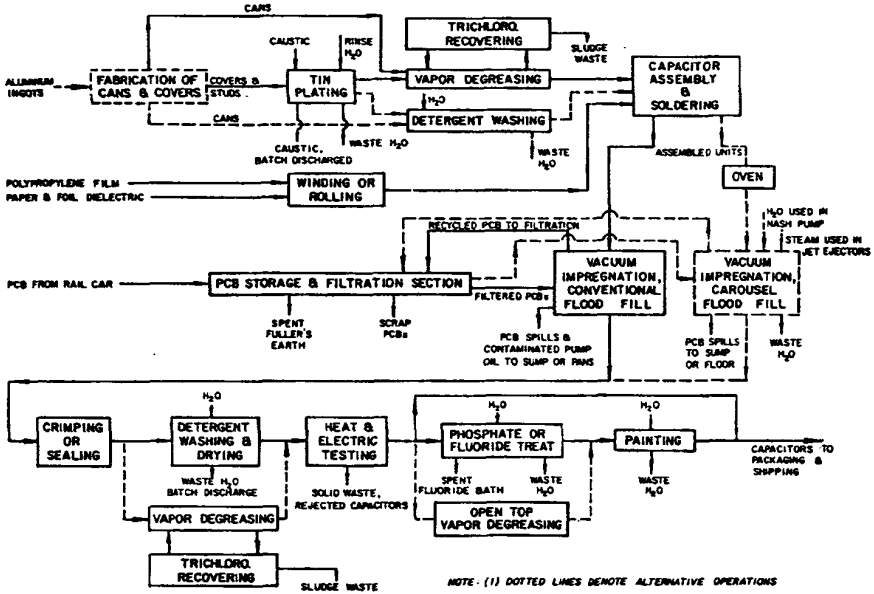

Figure 3.1.1.2-2
GENERALIZED FLOW DIAGRAM FOR THE MANUFACTURING OF SMALL CAPACITORS

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(1) Conventional flood filling of capacitors

This type of filling operation is used for impregnating large power and small industrial capacitors. Here the capacitors are arranged in baskets or in large tanks which are subsequently transferred into vacuum chambers. Vacuum is then drawn and the capacitors are kept under vacuum at an elevated temperature for a specific period of time in order to evaporate the moisture from the capacitor interiors. The temperature of the tank is next lowered and PCBs are introduced under vacuum. The capacitors are allowed to soak for some time after which they are transferred to the sealing or crimping station via mobile car, sealed, and excess PCBs are then drained. The sealed capacitors are next sent to vapor degreasing or detergent washing for cleaning the exterior of these units. The clean units are heat soaked and heat tested in an oven and then sent to 100% electrical testing.

Subsequent to electric testing, the capacitors with steel casings are pretreated prior to painting. The pretreatment is either vapor degreasing for painting in an electro-static field or it is several stages of phosphatizing and rinsing operations, prior to automatic spray painting, where water is used to scrub the vapors generated during painting. Most capacitors with aluminum casings are marketed unpainted. However, at some plants a portion of capacitors with aluminum casings are fluoride treated and then spray painted. The capacitors are next either air dried or dried in an infrared oven prior to packaging and shipping.

(2) Automatic Flood Filling Operation (Carousel)

In this method of capacitor impregnation, the assembled units are placed in ovens for the removal of moisture from the capacitor interiors. The baskets containing these capacitors are next transferred to the carousel chamber which is at the loading position. The carousel passes through 13 subsequent cycles consisting of

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various degrees of vacuum applications and then subsequent PCB filling and soaking positions. The PCBs are next drained out of the chamber, and the capacitor baskets are removed from the vacuum chamber and tilted to drain excess PCBs into a sump located adjacent to the carousel loading and unloading station. The capacitors are next transferred to the crimping or sealing stations. From this point on the remainder of the manufacturing steps are identical to those employed in conventional flood filling operation.

In general, vacuum in conventional flood filling operations is achieved via mechanical pumps, whereas vacuum in each automatic flood filling station is achieved via a vacuum pump and several stages of steam jet ejectors.

Rejected industrial capacitors are disposed of in 55 gallon drums either directly or after disecting. Rejected power capacitors which are flood filled are returned to the salvaging operation. Here the capacitor covers are cut on an end mill, the PCBs drained and the interiors examined to find the cause of the electrical failure. Where possible the rejected units are then repaired and reprocessed. Otherwise, the capacitor interior is discarded in a designated solid waste drum. The capacitor casing is sent to vapor degreasing and it is subsequently sold to a scrap dealer.

(3) Manifold Filling Operation

At some plants, large capacitors are filled by this method. Here, the capacitors are completely assembled, sealed and vacuum tested; then each unit is filled individually under vacuum through a manifold. The capacitor valve is next sealed, the exteriors spot cleaned with trichloroethylene and then these units are transferred into an oven where they are heat soaked for a given period of time prior to electrical testing. Those capacitors which pass the electrical tests successfully are vapor degreased, painted, dried, packaged and shipped. The rejects are returned to the filling station where

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the majority of the PCBs are retrieved through the fill valve under vacuum. The rejects are next transferred to the salvage operation.

Mechanical pumps are used throughout the system to achieve vacuum.

3.1.1.3 Raw Wastes

The raw wastes originating from these plants consist of scrap PCBs collected in sumps, drums and drip pans, contaminated vacuum pump oils, the fractionator bottoms from the trichloroethylene recovery, the caustic bath used, at some plants, for purposes of paint stripping, spent detergent wash and rinse water from capacitor or component cleaning operations, rinse water used in the welding and plating operations, steam condensate from jet ejectors, the seal water used in vacuum pumps, water used in phosphatizing and fluoride baths, water spray used in the paint booths, boiler blow downs and cooling tower blow downs.

Furthermore, in at least one plant in this category, water infiltrating at a subgrade elevator shaft creates an additional waste stream.

Solid wastes from these plants consists of scrap capacitors or capacitor interiors, floor dry and rags and newspapers used for cleaning spills, spent fuller's earth and other filtering media used for PCBs filtration and waterless cleaners used at some plants for hand cleaning purposes.

Non-product PCB discharges, their source and disposition are given in Table 3.1.1.3-1. Adequate data to quantify the various wastes generated at these plants is not available. Information on waste loads reported by some plants are given in Table 3.1.1.3-2.

3.1.1.4 Water Use

The water used at these plants is in the range of 12,500 to 1,260,000 gallons per day. In most plants, water is used primarily for once-through non-contact cooling in vapor degreasers, in pumps and in vacuum tanks. Plant 101 recycles their non-contact cooling water through a cooling tower.

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TABLE 3.1.1.3-1. NON-PRODUCT PCB DISCHARGES

Source	Plants 100	101	102	104	105	106
Vacuum pump exhaust	Air	Air	Air	Air	Air	Air
Evaporation & ventilation	Air	Air	Air	Air	Air	Air
Vapors from last stage of jet ejectors	None	None	None	None	Air	None
Personal hygiene	Sewer	Sewer	Septic tank	Incineration[1]	Incineration[1]	Sewer
Laundry water	None	None	Septic tank	None	None	None
Water phase from pump oil/water separator	Sewer	None	None	None	None	None
Sanitary & domestic water	Sewer	Sewer	Septic tank	Sewer	Septic tank leach field system	Sewer
PCB contaminated water	River	-	Treatment plant then river	River	River	Sewer
Non-contact cooling water	River	Recycled	Treatment plant then river	River	River	Sewer
Rainfall & surface runoff	River	Storm sewer	Treatment plant then river	River	River	Storm Sewer
Rinse water from component detergent washing	None	Dry well	None	River[2]	None	None
Water used in non-PCB electrolytic capacitor operations	None	None	Treatment plant then river	None	None	None
Ground water infiltration	None	None	None	Decant then to river	None	None
Controlled sink drains[3]	None	Sewer	None	River	River	None
Rinse water used in the caustic bath & welding	None	None	None	River	None	None
Water used in paint scrubbing	None	None	None	Decant then to river	River	None
Phosphatizing bath & rinse	None	None	None	None	River	None
Scrap oil in drip pans, drums & sumps	Incineration	Incineration	Incineration	Incineration	Incineration	Incineration
Spent fuller's earth, clay & filter cartridge	Incineration	None	Incineration	Stored on site	Stored on site	Landfill
Rinse water from dry-well	None	Incineration	None	None	None	None
Fractionator bottoms (sludge) from trichloro recovery	Incineration	None	Incineration[4]	Incineration	Incineration	Incineration
Spent detergent wash of capacitor exteriors	None	Landfill	None	None	Incineration	None
Spent fluoride wash	None	None	None	None	Incineration	None
Reject capacitors or capacitor internals	Landfill	Landfill	Landfill	Stored on site	Stored on site	Landfill
Newspaper, floor dry & rags	Landfill	Landfill	Landfill	Stored on site	Stored on site	Landfill
Caustic bath	None	None	None	Stored on site	None	None

Notes: [1]Sinks at the impregnation areas are contained; water from the sumps are sent to incineration.
[2]Rinse water from non-PCB, component washing operation.
[3]Employees are advised to use waterless hand cleaning material prior to washing their hands.
[4]Only liquids from this operation are sent to incineration. The sludge from this operation is sent to a municipal landfill.

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TABLE 3.1.1.3-2 QUANTITY OF WASTE LOADS
(lbs/ton of PCB used)

	Plants					
	100	101	102	104	105	106
Land Destined Waste	73[1]	129	65	-[4]	-[4]	-[5]
Wastes to Incineration	100	56	98	109	127	300
Spent Fuller's Earth to Incineration	4.1	None[2]	-[3]	-	-	Unknown

Notes:

(1) Reported as PCBs. We estimate an additional 175 lbs/ton of PCB contaminated solid material which is being landfilled locally.
(2) PCBs are filtered through packed Porocell cylindrical filters. The filter media has an estimated life cycle of 20 years.
(3) This plant uses clay for PCB filtration. The quantity of spent clay sent to incineration is not known.
(4) These plants store their solid wastes consisting of spent fuller's earth, rejected capacitors, rags and floor dry, on site. Plant 104 generates ten 55-gallon drums of waste and plant 105 forty 55-gallon drums of waste each week.
(5) The weight of materials sent to landfill is not known. However, this company reports that during 1974 approximately 650 capacitors were rejected. The rejected units were drained and then sent to a landfill.

MONS 052673

Process water used at various plants consists of water used in detergent washing, in ultrasonic washing, condensate from the steam jet ejectors, seal water from the vacuum pumps, water used in phosphatizing and in fluoride baths and rinses, and water used in caustic treatment and painting operations. Additionally, water is used for sanitary purposes and in some plants it is also used as boiler feed.

The quantities and types of water used at these plants are given below:

	Plants					
	100	101	102	104	105	106
Intake gallons/day	740,000	12,500	1,000,000[1]	1,260,000	480,000	336,500
Water Usage in gallons/day						
Non-contact cooling	655,000	3,000[2]	388,000[3]	1,195,000	387,000	326,500
Process water						
Rinse water from hot solder dip	200	-	-	-	-	-
Detergent washing & rinsing	-	8,000	-	25,000[4]	200	-
Phosphatizing baths	-	-	-	-	400	5,000
Water used in tin plating	-	-	-	-	12,000	-
Fluoride bath & rinse	-	-	-	-	50	-
Water used in painting					50	-
Pump seal water & steam condensate					44,000	-
Sanitary	44,900	1,500	52,000	10,000	65,000	5,000
Boiler feed make-up	40,000	-	-	30,000	15,000	-

Notes: (1) 560,000 gallons/day of this water is used as process rinse water in non PCB associated, electrolytic capacitor operation
(2) Make-up water
(3) It has been estimated that only 150,000 gallons of this water is associated with the plants PCB operation. The balance is used in the manufacture of Mica capacitors
(4) It includes water used in paint stripping and welding operations.

MONS 052674

3.1.1.5 Wastewater Treatment

The major in-plant PCB wastes which reach water streams originate in the impregnation areas. Due to the nature of water requirements in this industry, at some plants it is possible to significantly reduce the quantities of wastes entering the water systems by adoption of proper housekeeping measures. Since there is no demonstrated technology available for the terminal treatment of PCBs in wastewaters, there are no PCB wastewater treatment techniques currently in use at any facility. Details on wastewater treatment techniques used at various facilities for purposes of oil recovery or neutralization and on-going containment programs undertaken by some plants to prevent the entry of PCBs into the environment are given in Task II report, "Assessment of Wastewater Management, Treatment Technology, and Associated Cost for Abatement of PCBs Concentrations in Industrial Effluent", February 3, 1976, pages 46 through 52.

3.1.1.6 Effluent Composition

Effluent from plants in this category range from 2500 to 1,260,000 gallons per day. As indicated in the waste treatment section, these effluents are sent either into receiving waterways or into municipal sewers without any PCB treatment. Available information on effluent flow rates and their PCB contents, for most plants in this category, are given in Table 3.1.1.6-1. More detailed effluent information were obtained on four plants and Table 3.1.1.6-2 compares the discharges from these plants. Table 3.1.1.6-3 lists PCB concentration of the plant intake water from various sources.

It is of interest to note that one plant (plant 100) reported large variations in the PCB content of the receiving waters even at the time when the plant was not in operation. They attributed the variations to storm conditions, stirring-up the sediments from the bottom of the river and greatly increasing the PCB concentration in the water phase.

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TABLE 3.1.1.6-1 RANGE OF FLOW RATES & PCB CONCENTRATION IN EFFLUENTS FROM CAPACITOR MANUFACTURING PLANTS

Plant No.	Outfalls	Effluent Flow Rate gal/day	Effluent PCB Content ppb avg/max	Effluent PCB Content lbs/day avg/max	Disposition of effluent
100	001	800,000	17/55	0.1134/0.3670	River
101	None	9,000	161/161	0.0121/0.0121	Sewer
102	001	807,000	9	0.0605	River
	002	165,000	3.2	0.0044	River
	003	36,000	3.4	0.0010	River
104	Major outfall	1,060,000	21	0.1856	River
	Cooling water & roof drains	100,000	7.8	0.0065	River
	Lab & roof drains	32,000	4.4	0.0011	River
	Compressor cooling water	72,000	3.7	0.0022	River
	Paint strip rinse	50	4800	0.0002	River
105	Major outfall	650,000	370	2.0058	River
	From spray paint booths	1,500[1]	13,300	0.1664	River
106	None	336,500	26.6	0.075	Sewer
107	None	150,000	1900/4000	2.3769/5.7546	Sewers
108	Cooling water & boiler blowdown	48,000	45/108	0.0180/0.0432	River
	Cooling water	129,000[2]	338/705	0.3636/0.7585	Sewer
	Roof runoff	2,900	1360/2370	0.3290/0.0573	River
	Storm runoff	unknown	3/11	- -	River
109	001	100,000	57/83	0.0475/0.0692	River
110	None	2,570	821	0.0176	Sewer
111[3]	None	18,000	8.7	0.0013	Sewer
112[3]	None	10,224	130	0.0110	Sewer
113	001	12,000	14.3	0.0014	River
126	None	580	6200[3]	0.03	Sewer

Notes: (1) Discharged once every 4-5 weeks.
(2) Contains 10,000 gpd sanitary sewage and 8000 gpd of surface water infiltration
(3) These facilities recycle most of the non-contact cooling water used at the plant. These effluents consist of a small fraction of the cooling water plus their sanitary discharge.

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TABLE 3.1.1.6-2

Comparison of Discharges

Plant	100	102			104				105
Outfall	001	001	002	003	002	003A	003B	006	004
pH	7.3	7.4	7.3	7.2	6.5-12.0	5.5-9.8	4.0-9.1	6.8-11.6	5.5-8.6
TSS, mg/l	3	16.6	1.54	2.8	5.2	4.7	4.0	3.1	9.5
PCB, ppb	17	9	3.2	3.4	21	7.8	4.4	3.7	370
Oil & Grease, mg/l	UK	3.10	3.38	2.18	7.20	14.40	30.70	2.66	12.8
Aluminum, mg/l	UK	ND	ND	ND	0.15	0.06	0.11	2.0	
Lead, mg/l	<.05	UK	UK	UK	UK	UK	UK	UK	UK
Copper, mg/l	<.003	UK	UK	UK	0.03	0.02	0.04	0.03	UK
Chromium, mg/l	<.005	UK	UK	UK	0.003	ND	ND	ND	0.03
Phenols, mg/l	<.001	UK	UK	UK	UK	UK	UK	UK	UK
Iron, mg/l	<.19	UK	UK	UK	0.29	0.30	0.34	1.66	0.52
BOD, mg/l		4.37	2.45	1.7	UK	UK	UK	UK	UK

ND - Non detectable
UK - Unknown

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Table 3.1.1.6-3

Intake Water PCB Concentration

Plant	100	101	104	105	106	111	112
Source	Municipal	Municipal	River	Well Water	Municipal	Municipal	Municipal
PCB, ppb	0.09-2.5	4-7	57.0	40.0	0.25	1.0	1.0

MONS 052678

3.2 Askarel Transformer Manufacturing Industry

All plants in this category manufacture transformers using mineral oil as the dielectric fluid. This dielectric fluid is the principal impregnant used at these facilities. PCB transformer oils (blends of 60 to 70 percent Aroclor 1254 or 1242 and 40 to 30 percent trichlorobenzene) are used in only 5-10 percent of these plants' manufacturing volume.

In general, a transformer consists of a core and coil immersed in a dielectric fluid. There are two broad classifications of transformers: distribution transformers, which are used to step down voltages, and power transformers, which are used primarily to step up voltages. The precipitation power supply units can be actually classified as a third class of askarel transformer. However, the larger plants in this category have only two manufacturing departments — distribution and power; and they manufacture the precipitator transformers in their distribution transformer department. The following types of askarel transformers are manufactured at these plants:

A. Askarel Distribution Transformers

1. Network (Receive up to 14,400 volts and deliver 120, 240 and 480 volts)
2. Pad - mounted (Receive up to 14,400 volts and deliver 120, 240 and 480 volts)
3. Pole - mounted (Receive up to 14,400 volts and deliver 120, 240 and 480 volts) The application of these transformers in power distribution systems places a great premium upon their reliability and high overload capability.
4. Precipitator power supply (Receive 480 AC volts and deliver 50-60 kilovolts low amperage DC) These units are generally installed close to hot gas stacks in an atmosphere that would be a fire hazard to oil-insulated transformers and a corrosive hazard to open dry-type transformers. Sealed dry-type transformers are impractical for high-voltage DC.

MONS 052679

Voltages listed cover the majority of askarel distribution transformers. Product scope includes up to 34,500 primary volts and virtually any secondary voltage, 34,500 and below.

Quantities of askarel used in this class of transformers are in the range of 500 to 5,000 lbs. in each unit depending on the rating and the size of the transformer.

A great majority of distribution type transformers have provision for venting. Many of these units are equipped with spring loaded venting devices which vent upon a pressure excursion, and diaphragm rupture discs are offered as a customer option.

B. Askarel Power Transformers

1. Secondary substation
   (a) Load center units
   (b) Secondary substation generation units
   (c) Switchboard units
   (d) Internal units
   (e) Motor control units

   These 5 comprise the largest group of askarel-insulated transformers and they find widespread application in the automobile, paper, chemical, textile, steel, nonferrous metal, cement, mining and petroleum industries. They are used in commercial and public buildings, such as schools and hospitals; in defense and nuclear energy installations; and by private and public utilities.
2. Master unit substation
3. Primary unit substation
4. Limited ampere substation
5. Industrial furnace

MONS 052680

Furnace transformers used in the hot, dirty atmosphere in proximity to glass melting and induction furnaces, which require high current, low voltage power supplies (receive up to 15,000 volts and contain 2000 to 4000 lbs. of askarel each). Existing technology does not permit construction of sealed dry-type transformers for these power ratings.

6. Rectifier

Rectifier transformers used for large rolling mills and DC industrial power supplies (receive up to 15,000 volts AC and deliver low voltage high amperage DC. Each unit contains about 19,000 lbs. of askarel). These units are covered by the same comments given for industrial furnace transformers.

7. Transportation

Railroad transformers used on-board in electric locomotives or multiple unit electric railroad cars (receive up to 25,000 volts and contain 700 to 2400 lbs. of askarel in each unit depending on the rating and size of the transformers).

(a) Third rail

These transformers are used for rapid transit systems, and are basically serving a rectifier function

(b) Locomotive

Prior to 1932, all on-board transformers were open dry type. Because of problems with them, railroads went to askarel-insulated transformers. The changes in locomotive design since the 1930's would not now accomodate open dry-type transformers as replacements for askarel units. A recent trend has been to replace askarel by oil units, and this will continue unless new Department of Transportation regulations require nonflammability.

MONS 052681

However, since a tunnel fire in 1940 caused by an oil filled locomotive transformer, Penn Central will not allow any oil containing transformer equipped locomotive into New York City.

(c) Multiple-unit car (MU)

These transformers are mounted under the flat-bed of passenger cars. They ride along in this location, about 8 inches above the rail, at speeds up to 150 mph. The transformer must be ruggedly built to withstand the impact of flying debris and constant vibration. Power to the cars is brought in through an overhead catenary and is fed to the underside of the car where the transformer, controls, and propulsion equipment are located.

Space and weight are critical in this application. There are only about 33 inches above the rail. The width of the transformer is limited by the width of the car.

Only oil- or askarel-insulated units would provide the required performance levels in the space available. As with locomotive applications, present Department of Transportation regulations do not restrict the use of flammable liquids, and the use of askarel units has been dictated largely by the economic considerations of fire insurance rates, and by Penn-Central safety regulations.

8. Reactors

These units provide reactance (receive up to 15,000 volts under normal operating conditions. During normal operating conditions, they deliver volts and current as received. During power surges they choke the voltage and deliver the normal output).

9. Grounding,transformers (receive up to 15,000 volts).

MONS 052682

3.2.1 Transformer Manufacturing Plants

There are thirteen companies in the U.S. which manufacture askarel transformers at eighteen plants. The name and location of these plants are given in Table 3.2.1-1. Some plants manufacture various types of transformers described above and others manufacture only one specific line of transformers.

All plants in this category were contacted to obtain information on their waste water. Detailed information was obtained on two plants which were visited. The largest U.S. transformer plant (based on quantity of PCB use) was not visited because of lack of cooperation. The data base represents approximately 20 percent of the 1974 PCB usage for transformer application. The PCB usage in this category was 12,000,000 lbs. in 1974 (equivalent to 15.0 to 17.0 million lbs. PCB transformer oil). The PCB usage in individual plants is considered by these companies to be confidential information. The range of plant PCB usage was 975 fold in 1974. Plant ages range from three to eighty-five years.

The amount of askarel used in individual transformers ranges from 40 to 1500 gals. (516 to 19,350 lbs.) with an average of about 232 gals. (3,000 lbs.). A sketch of a large substation transformer is shown in Figure 3.2.1-1. G.E. estimates that the total askarel-insulated units that have been put into service in the United States since 1932 is 135,000, and virtually all of these units are still in service. The lifetime-before-failure is often longer than 30 years, and almost all units that do fail are rebuilt and returned to service. The current production rate of askarel transformers is about 5,000 units per year.

3.2.1.1 Askarel Handling

Few plants in this category purchase PCBs and trichlorobenzene and do their own compounding. Most plants purchase pre-compounded askarel from Monsanto. Smaller plants purchase their askarel in 55 gallon drums, filter the askarel and pump directly into the transformer tanks. To large plants askarel is shipped via rail cars. Rail cars enter in a designated area at the plant site. Askarel is then pumped from the rail cars into the raw askarel storage tank. Any spillage in this area is cleaned by rags or floor dry. The raw askarel

MONS 052683

Table 3.2.1-1

U.S. Transformer Manufacturing Industry Using PCBs

Company Name	Location of the Plant
Westinghouse Electric Corp.	South Boston, Va. Sharon, Pa.
General Electric Company	Rome, Ga. Pittsfield, Mass.
Research-Cottrell	Finderne, N.J.
Niagara Transformer Corp.	Buffalo, N.Y.
Standard Transformer Co.	Warren, Ohio Medford, Oregon
Helena Corp.	Helena, Alabama
Hevi-Duty Electric	Goldsboro, N.C.
Kuhlman Electric Co.	Crystal Springs, Miss.
Electro Engineering Works	San Leandro, Calif.
Envirotech Buell	Lebanon, Pa.
R.E. Uptegraff Mfg. Co.	Scottsdale, Pa.
H.K. Porter	Belmont, Calif. Lynchburg, Va.
Van Tran Electric Co.	Vandalia, Ill. Waco, Texas

MONS 052684

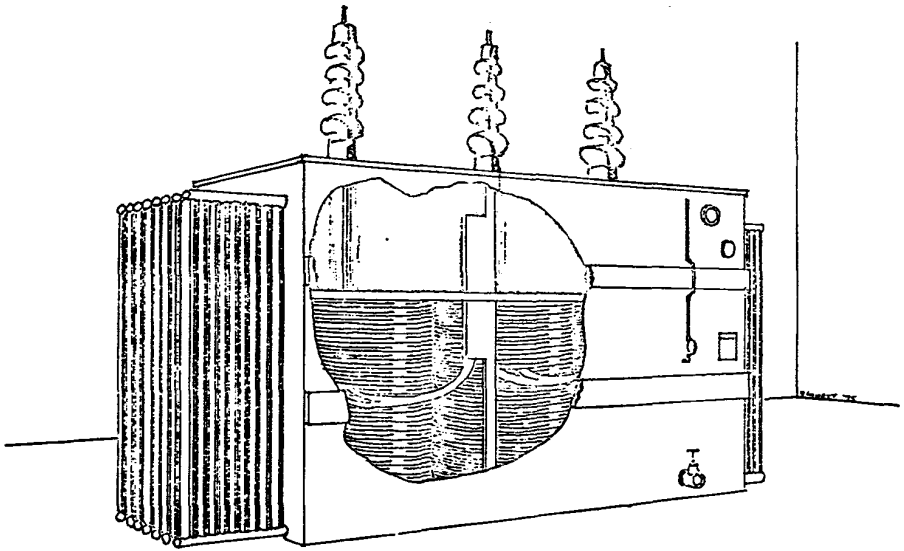

FIGURE 3.2.1-1. SUBSTATION TRANSFORMER

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is next filtered through attapulgite clay or fuller's earth and is often passed through a plate and frame type filter for final cleaning and then stored in the finished product storage tanks. Spent clay or fuller's earth from this operation is drummed and stored on site or sent to a landfill.

In some plants, the entire storage area is located within dikes and curbs designed to contain at least the contents of the largest single tank plus sufficient free board to allow for precipitation.

At most plants the askarel is distributed from the tank farm area to the filling station, but at one plant (Plant 103) the finished askarel is next trucked from a covered/curbed storage area to an uncovered/bermed tank farm area. Here the truck enters a shelter area, and the askarel is then pumped from the truck into distribution storage tank.

Recycled askarel from the manufacturing operations is generally returned through pumps into a storage tank or into 55 gallon drums and from there it is either filtered for reuse or is sent to incineration if it is proved to be defective.

3.2.1.2 Process Description

Most plants manufacture all the hardware and components necessary for the transformer assembly. The transformer interiors and the containers are brought to the askarel filling stations where transformers are assembled, filled and sealed.

The filling operation is done in a designated station. At plants where small quantities of askarel are handled, spills and drips are cleaned via floor dry or rags. At plants where large quantities of askarel are handled, filling operation is conducted on gratings located on sumps. All drainage is directed into these sumps. The sumps are inspected and cleaned periodically. All scrap askarel from sumps is pumped into drums and sent to incineration.

Various transformer assembling and filling procedures are being practiced throughout this industry. In general, all transformer assembling and filling operations consist of a predrying step for removing moisture

MONS 052686

from the transformer interiors, several stages of askarel filling and askarel topping, addition of electrical connections and bushings, electrical testing and sealing.

At plants where relatively small quantities of askarel are used, the assembly and filling procedure for distribution and power transformers are alike. Some plants manufacture only a given size of transformers (single tank size operations). At larger plants different assembling and askarel filling procedures are employed for various transformer subcategories. Some of the askarel transformer assembling and filling procedures practiced within this industry are described below.

3.2.1.2.1 Assembly and Askarel Filling Procedure for the Distribution and Power Transformers

A. Vapor Phase Drying Prior to Filling

This procedure is primarily used in the filling of network and pad-mounted transformers. The drying of the transformer internals is a vapor phase treatment with a kerosene-like petroleum distillate. A schematic flow diagram depicting this system is given in Figure 3.2.1.2.1-1. The assembling steps for these transformers include the following:

- First the transformer interiors are placed in large vacuum chambers heated with steam coils. The petroleum liquid is admitted, vacuum and heat are applied. The petroleum vapors rise to be condensed on the interiors, exchanging latent heat for sensible heat and raising the temperature of the interiors. After a specific time the liquid is pumped out; vacuum and heat are continued to dry the internals.
- The internals are next removed and placed in their own containers and flushed with askarel at atmospheric pressure. The askarel is kept in the tank until the liquid temperature is lowered to a preset level at which time it is pumped out of the tank. The purpose of askarel flushing is to chill the transformer interiors prior to final filling.

MONS 052687

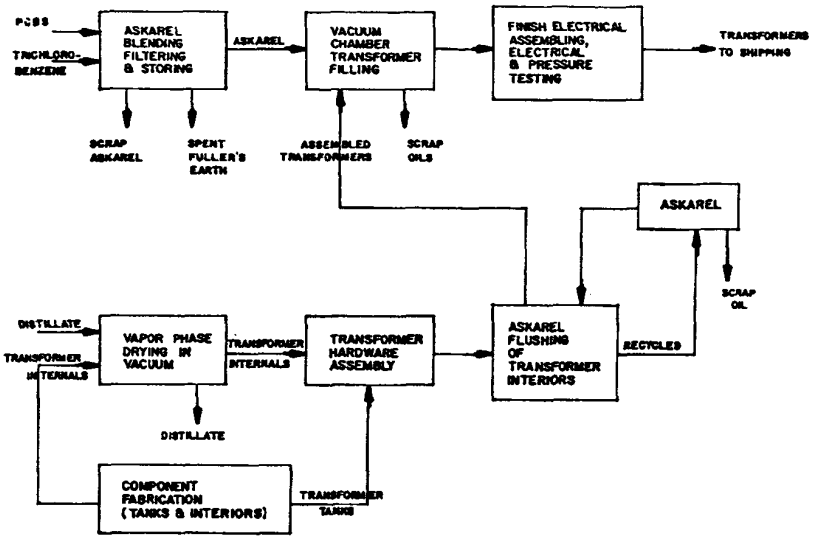

Figure 3.2.1.2.1-1
TRANSFORMER FILLING WITH VAPOR PHASE PREDRYING OF INTERIORS

MDNS 052688

- The tank is next placed in a designated vacuum chamber. Vacuum is drawn and then fresh askarel is metered in slowly to avoid foaming or flooding.

- The vacuum chamber is next opened, the electrical connections are made and the liquid level in the tank is then brought to the operating level at atmospheric pressure. The transformer tank is then crane lifted and lowered onto conveyors and sent to specified test stations for a series of electrical tests before the transformer is completely sealed.

- If a transformer fails the electrical tests, it is returned; the askarel is drained and reprocessed. Otherwise, the transformer is sent to cover welding operations.

- The tank is next lifted and sent back via conveyor belts to the filling station where it is topped with askarel through an access overhead pipe. The transformer is next pressure tested for leaks. The bottom drain valve is then sealed and the top opening is pipe fitted and sealed. Sealing is accomplished primarily by teflon tape. However, for some transformers, the sealing is done by an air cured sealant at customer's request.

B. Oven Drying of Transformer Internals Prior to Filling

This procedure is used primarily in the assembly of pole type or precipitator transformers. The drying of internals for this category of transformers is accomplished in a convection oven. The internals are then placed in their own casings and the bushings and electrical connections are next made. Vacuum is then applied via a mechanical pump and the tank is filled with askarel while the transformer internals are still at a predetermined elevated temperature. Exhausts from this operation are pulled through a venting system.

MONS 052689

Most transformers in this subcategory have gasketed covers with barrel band type connections. Subsequent to the filling operation, the transformers are sealed and pressure tested for leaks. The large units are liquid pressure tested while the smaller ones are air pressure tested. A schematic flow diagram depicting this system is shown in Figure 3.2.1.2.1-2.

The contaminated oil from the vacuum pump is treated as waste askarel and is sent to incineration.

C. Oven Drying of Assembled Units Prior to the Filling

This procedure is used primarily in the assembly of the precipitator transformers. Here the transformer internals are placed in their own casings, the covers are welded on the casings and the assembled tank is placed in the convection oven all sealed. At an elevated temperature, vacuum is applied at predetermined intervals. The tank is then transferred to the filling station where askarel is added through an upper pipe opening under vacuum. Both the top piping and the drain valve are next sealed and the unit is then pressure tested. A schematic flow diagram depicting this system is shown in Figure 3.2.1.2.1-3.

D. Procedure for Assembling the Askarel Filled Power Transformers

The same procedure is used to assemble all types of askarel filled power transformers. The transformer internals are dried in sealed vacuum tanks, then they are placed in their own containers and the cover is welded and sealed. The unit is then pressurized and checked for leaks by a helium detector. The tank is next transferred to the filling station where low vacuum is drawn for a period of 24 hours. The askarel line is then connected and the tank is filled slowly while under vacuum up to the operating level. The unit is then sealed and sent to electrical testing. After the tests the transformer is returned back to the filling station where it is nitrogen pressure tested just prior to shipping. The schematic flow diagram depicting this system is shown in Figure 3.2.1.2.1-2.

MONS 052690

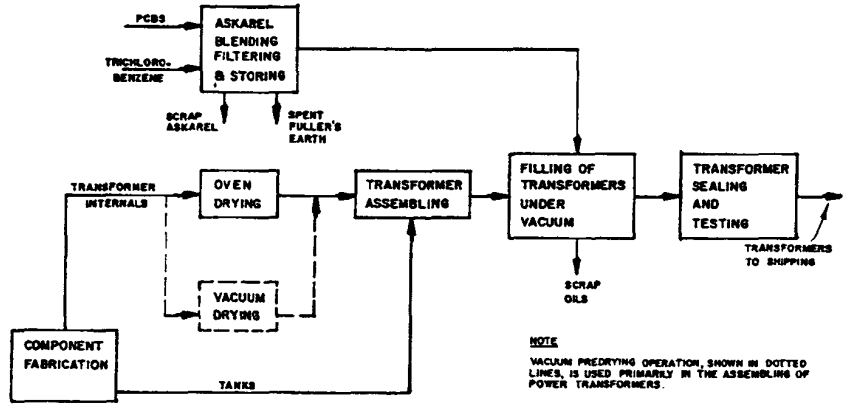

Figure 3.2.1.2.1-2
TRANSFORMER FILLING WITH OVEN OR VACUUM CHAMBER PREDRYING OF TRANSFORMER INTERNALS

MONS 052691

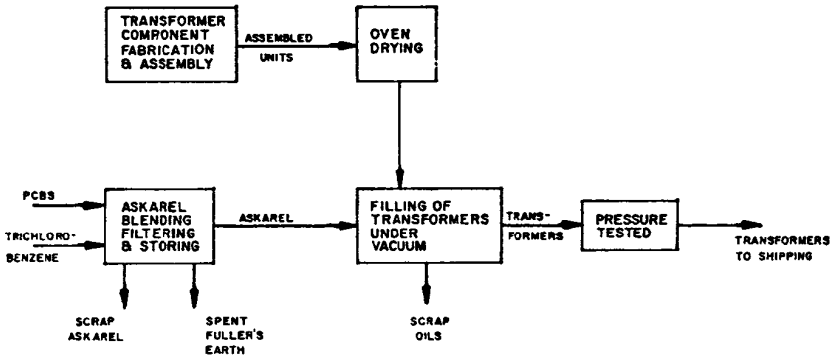

Figure 3.2.1.2.1-3
TRANSFORMER FILLING OPERATION WITH OVEN PREDRYING OF ASSEMBLED HARDWARE

MONS 052692

All power transformers have air space on the top and are equipped with an air cooled circulation system. Additionally, each unit has a spring loaded relief valve as standard equipment. These transformers have a greater potential for environmental contamination through the vent system, via leaks on the pump and the valves.

3.2.1.3 Raw Wastes

In general, the process raw wastes from these plants consist of waste askarel collected in sumps or pans at the filling stations, contaminated vacuum pump seal oil, contaminated kerosene-like petroleum distillate (used in at least one plant in the vapor phase drying operation), contaminated askarel used for transformer interior flushing and contaminants in the plant effluent.

Additionally, plant 103 has a unique waste stream consisting of contaminated ground water which is being pumped from three caissons at the plant site. Plant 103 also has a bleedwater discharge from their incineration system.

Solid wastes from these plants consist of rags and floor dry used for miscellaneous cleaning purposes and spent clay used for Aroclor filtration. Additionally, at plant 103 it includes the sludge from oil/water separators.

Non-product PCB discharges are shown in Table 3.2.1.3-1. Estimates on the quantities of raw waste generated in two plants which were visited are given below.

	Plants	
Quantities of Waste Loads	103*	114
Wastes to incineration, lbs/ton of PCB used	115	98.0
Solid waste material stored on site in 55 gallon drums	135 units	Unknown

3.2.1.4 Water Use

Water is not an essential component of the transformer manufacturing process. PCB wastes which reach water streams at these plants are due to inadvertent occasional loss during handling and residuals accumulated

MONS 052693

TABLE 3.2.1.3-1

NON-PRODUCT PCB DISCHARGES

Source	103	114
Plant exhaust	Air	Air
Incinerator exhaust	Air	None
Personal hygiene and sanitary water	Sewer	Sewer
Ground water pumped through caissons	To oil separators then river	None
Water used at plant	To oil separators then river	Sewer/river
Contaminated oils and waste PCBs	incineration	Incineration
Floor sweepings and rags used for cleaning	decapsulator	Incineration
Rejected transformer interiors for copper recovery	decapsulator	Stored on site
Contaminated and defective empty drums	To steel furnace in steel mill	Shipped to the company which handles their contaminated oils
Sludge from the oil separator	Stored on site	None
Clay used for askarel filtration	Stored on site	None

MONS 052694

around the drainage systems from past operations when no precautions were taken in handling and disposal of PCBs.

This category uses water primarily for non-contact cooling purposes in vacuum pumps, compressors and at some plants as contact cooling in their welding and plating operations and in phosphatizing of the steel surfaces prior to painting. All contact cooling operations listed above are primarily non-PCB related operations. Only plant 103 has a PCB related process water which consists of the water used in their waste incineration system for quenching the hot gases from the reaction section. Plant 103 is also the major water user in this category.

In most smaller plants all cooling is accomplished by air. At these plants water is primarily used for hygiene and sanitary purposes and for occasional compressor or pump cooling purposes. The only water that comes into contact with PCBs at these latter plants is that used for personal hygiene. The types and quantities of water used at two plants visited are given below.

	Plant No.	
Water Usage in Gallons/day	103	114*
Non-contact cooling	1,646,000	38,000
Process water		
. Contact cooling	183,000	None
. Detergent washing	2,000	None
. Incineration quench	122,000	None
Hygiene	Unknown	300
Boiler make-up	Unknown	200
Sanitary	Unknown	9,000
Non PCB related		
. Water used in a lab	Unknown	500
. Water used for external cleanups	None	4,000

*Breakdown of the water usage was estimated.

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3.2.1.5 Wastewater Treatment

There are no effluent treatment techniques in practice at any plant in this category for the removal of PCBs. However, in 1972, a John Zink designed thermal oxidation incinerator was erected at plant 103 to safely dispose of PCBs. A schematic flow diagram of this unit is given in Figure 3.2.1.5-1. This unit consists of two steam atomized burners and a long cylindrical chamber to provide residence time for thermal degradation. Following the chamber is a water spray quench pot and a counter current packed scrubber column located at the base of the stack.

The waste oils are brought into the incinerator site in 55 gallon drums or by truck trailers. These waste oils are next pumped from the drums or from the trailers into the incinerator feed tanks. The steam atomizing burners inject the combustible liquid wastes into the combustion section with air, in such a manner to create a vortex type turbulence. This produces high heat release and effective combustion promoting the thermal degradation process. After combustion, the waste gases proceed through the oxidation chamber which provides 3 to 12 seconds of residence time at temperatures 1600 to 1800°F for the degradation reactions to go to completion. The flue gases from the chamber pass through a quench pot which contains a series of water sprays to cool the gases. An induced draft fan then forces the cooled gases through the packed bed scrubber column. Here, acidic ions produced during the combustion process are absorbed in the scrubber liquor. The scrubber liquor is then neutralized and disposed into the sewer.

A high temperature decapsulator has been incorporated in the thermal oxidizer unit for solid incineration and copper recovery. The exhaust of this unit is routed to the upper end of the oxidizer chamber.

Details on wastewater treatment techniques utilized at one facility (plant 103) for purposes of oil recovery and on-going containment programs undertaken by two plants (plants 103 and 114) in order to prevent the entry of PCBs into the environment are covered in the Task II report, "Assessment of Wastewater Management Treatment Technology, and Associated Costs

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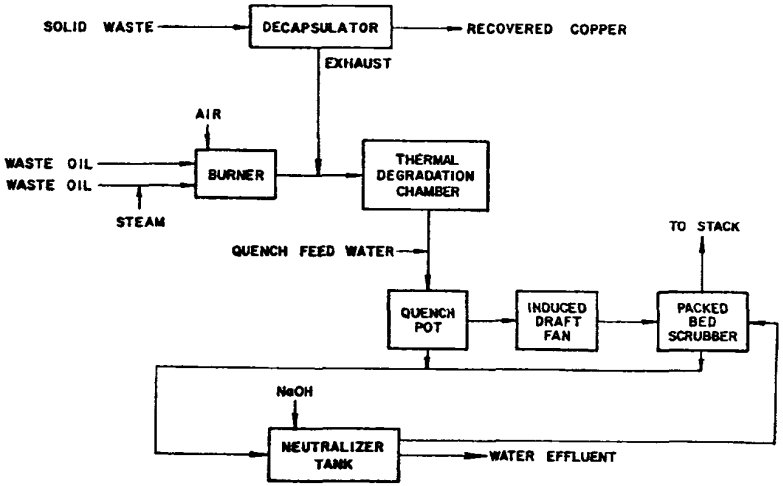

Figure 3.2.1.5-1. PROCESS FLOW DIAGRAM FOR THERMAL OXIDIZER INCINERATOR AT PLANT 103

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for Abatement of PCBs Concentration in Industrial Effluents", February 3, 1976, pages 71 through 75.

3.2.1.6 Effluent Composition

Effluent flow rates and PCB contents are available from the three plants which discharge into the rivers and from two plants which discharge primarily into sanitary sewers. Detailed effluent composition is available only on Plant 103. This information is given in Tables 3.2.1.6-1 and 3.2.1.6-2, respectively.

The remaining plants in this category which discharge to sanitary sewers report that their water usage, for reasons other than for sanitary purposes, is minimal. However, they have no data available on the quantities and composition of water discharged.

3.2.2 Askarel Transformer Repair Industry

A total of 13 companies repair transformers containing PCBs at a total of 131 locations. The current industry structure has been identified, and several potential problems were noted. No estimates have been made of the pollution which occurs from this industry.

3.2.2.1 Transformer Inspection and Maintenance

Askarel transformers are very reliable and have lifetimes that range up to 40 years. The failure rate of askarel filled transformers has been estimated by the manufacturers to be 0.2 percent per year. Failure occurs primarily due to the degradation of the PCB fluid caused by electrical arcing within the transformer.

Nine electrical utilities were contacted to determine their inspection and repair procedures. All of these companies have some type of program, usually informal, for the checking of their transformers. In most cases this consists of a simple annual inspection which may include a general cleaning operation of the facilities adjacent to the hardware (e.g., the vaults may be cleaned and vacuumed). Inspection involves looking for evidence of leaks. One utility performs an annual power factor test on the windings, and if this test indicates a problem in the transformer, then its dielectric fluid

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TABLE 3.2.1.6-1

PCB CONCENTRATION IN EFFLUENTS FROM TRANSFORMER MANUFACTURING PLANTS

Plant No.	Discharge Designation	Effluent Flow Rate Gal/Day	Effluent PCB Content ppb Avg/Max	Effluent PCB Content lb/day Avg/Max	Disposition of Effluent
103[1]	005	1,310,000	4.9/120	0.0535/1.311	River
	006	550,000	7/75	0.0321/0.344	River
114	None	50,000[2]	Unknown	Unknown	Sewer
	None	2,000[2]	Unknown	Unknown	River
115	002	36,000	<1/2	<0.0003/0.0006	River
	003	24,000	2/113	0.0004/0.0220	River
	004	150,000	<1/3	0.0013/0.0039	River
116[3]	#1	252,000	3.4/11	0.0071/0.0231	River
	#2	378,720	2.1/3.8	0.0066/0.0120	River
	#3	504,000	8/19.1	0.0336/0.0803	River
117	Batch discharge	13,500	28.6/unknown	0.0032/unknown	Sewer

Notes: (1) This plant has other discharges out of their properties. Discharges listed above are those associated with PCB related operations.

(2) Estimated.

(3) Discharges designated as #1, #2, and #3 are the combined effluents from their power house, and one each from their two manufacturing areas, respectively. According to the plants' Corps of Engineers permit application form, filed in July 1971, this plant has 13 outfalls.

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TABLE 3.2.1.6-2

INFLUENT AND EFFLUENT COMPOSITIONS OF PLANT 103

	Incoming Municipal Water	Outfall 005	Outfall 006
Average flow rate million gpd	1.86	1.31	0.55
pH yearly average	6.4	7.7	5.5
pH min.-max.	—	6.4-8.0	3.1-7.1

		Avg/Max Conc.	Avg lbs/day	Avg/Max Conc.	Avg lbs/day
Alkalinity, mg/l	14	25/25	273	15/20	69
BOD, 5-day, mg/l	2	3/3	28	27/30	124
Chemical oxygen, mg/l	9	23/34	251	75/92	344
TS, mg/l	69	70/70	765	364/497	1671
TDS, mg/l	68	67/67	735	341/483	1565
TSS, mg/l	1	3/9	31	23/30	106
TVS, mg/l	34	19/22	208	89/96	408
Ammonia, mg/l (AN)	0.05	<0.2/1.0	<2	2.8/3.0	13
Kjeldahl Nitrogen, mg/l	0.45	0.8/1.0	9	4.6/5.1	21
Nitrate AsN, mg/l	0.15	0.55/0.9	6	0.98/1.02	5
Phosphorus Total, mg/l	0.01	0.04/0.05	<1	54/124	248
Color (As P)	30	25/30	-	30/30	-
Turbidity, mg/l	<25	<25/<25	-	<25/<25	-
Total hardness, mg/l	44	31/44	340	33/44	152
Organic Nitrogen, mg/l	0.5	0.6/0.7	6.6	1.8/2.0	8
Sulfate, mg/l	9.0	14/18	153	9.0/9.0	41
Sulfide, mg/l	<0.1	<0.1/<0.1	<1.0	<0.1/<0.1	<0.5
Chloride, mg/l	6	6/8	61	11/13	50
Cyanide, µg/l	<0.00	0.00/<0.01	0.04	<0.00/<0.00	<0.02
Fluoride, mg/l	0.16	-	-	9.5/12.0	44
Aluminum - total, µg/l	100	500/550	5	200/200	0.9
Boron - total, µg/l	70	-	-	9/70	0.04
Calcium - total, mg/l	6.5	7.0/7.5	77	7.7/8.0	35
Chromium - total, µg/l	<10	30/30	0.3	310/350	1.4

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TABLE 3.2.1.6-2 (CON'T)

	Incoming Municipal Water	Outfall 005		Outfall 006	
Cobalt, total, µg/l	<7	4/4	0.04	-	-
Copper - total, µg/l	500	20/500	0.2	30/500	0.13
Iron - total, µg/l	330	150/330	1.6	3200/3500	15
Lead - total, µg/l	<30	<10/30	<0.1	80/90	0.36
Magnesium - total, µg/l	7	3/7	36	3/7	16
Manganese - total, µg/l	200	50/200	0.5	120/200	0.55
Mercury - total, µg/l	<1	<1/<1	<0.004	2/2	0.01
Molybdenum - total, µg/l	<7	-	-	90/99	0.41
Nickel - total, µg/l	100	<10/100	<0.1	10/100	0.04
Potassium - total, mg/l	1.1	0.88/1.10	9.6	0.99/1.1	4.5
Silver - total, µ	<10.0	-	-	2.0/2.0	0.009
Sodium - total, mg/l	5	6/10	66	25/30	117
Tin - total, µg/l	<7	7/10	0.07	-	-
Titanium - total, µ	2	-	-	3/3	0.01
Zinc - total, µg/l	30	70/75	0.76	730/800	3.4
Oil & Grease, mg/l	1.0	2/10	21	3.0/9.0	13.7
Phenols, µg/l	3	101/110	1.1	168/180	0.77
Surfactants, mg/l	<0.02	0.11/0.15	1.2	0.22/0.30	1.0
Chlorinated hydrocarbons, mg/l (except pesticides)	<1.000	1.000/5.000	11	1.000/1.000	4.6
PCBs, µg/liter	-	4.9/120	0.05	7/75	0.03

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is tested - at least this is the theoretical method of operation since the company has only two PCB-type transformers in use and neither has ever failed the power factor test. Another company measures the operating temperature of the units and makes a visual inspection for leaks; this company also claims that transformers located in the generating facility are inspected daily (visual inspection) and that units located in vaults are checked at least weekly. While most major inspections are carried out annually, the range of time intervals between inspections is 6 months to 18 months, with one company saying that they inspect at least once every 2 or 3 years, and another saying that substation transformers are inspected weekly.

These companies perform no sampling and analysis work on their askarel transformers. One company has annual inspection of all transformers, but only the mineral oil-type units have samples withdrawn for analysis to see if there is deterioration or contamination. A company which used to perform power-factor tests until about 8 years ago has since abandoned such tests and does not withdraw askarels for analysis.

Servicing of transformers is only rarely performed in-house. The response of most companies was that servicing of askarel-type transformers had yet to be required. One company did its own servicing up until 8 or 10 years ago, but since then, because of the special handling problems associated with askarels, such work has been farmed out to G.E. and Westinghouse service centers. The general trend seems to be that major servicing is more likely to be done at special facilities outside the utility companies while minor servicing, such as the repair of small leaks is taken care of at the transformer site by the utility.

More than half of the companies have not scrapped transformers in the past five years, and most have not scrapped any in the past 10 years. One utility company has had no transformer failures in 20 years (except for a minor leak of less than 1 gallon ten years ago). These companies have no specific disposal methods for such instances. One company said that scrap transformers are handled through a local junk company and that askarel disposal is the junk company's problem. A company which says it has scrapped no transformers says that when the PCB capacitors fail they are shipped back to

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the manufacturer; presumably, though it was not stated directly, failed transformers would also be returned to their manufacturers. One company which is proud of its disposal practices has disposed of 200 to 400 gallons of askarel per year since 1970 (most of it comes from failed capacitors); until this year it was all sent to Monsanto for incineration, but starting this year they have been sending it to Sheffield, Ill., where it is dumped in a landfill that has been approved by EPA for the disposal of radioactive wastes. This company stated that many utility companies dump their PCB-related wastes in local landfills.

There has been little PCB lost to the environment through the safety release valve on the transformers. The consensus response was that if the valve released there would be askarels "all over the place". The spokesman for one utility did not know whether the transformers they used had safety valves. One company said that a transformer vented several years ago when a fuse that was supposed to protect the transformer did not protect it.

Very seldom is a failed transformer scrapped. However, sometimes the repair work needed in a failed unit could be rather extensive and very costly. The owner of the unit may request to scrap his unit. If the repair shops scrap a transformer, they follow the procedure recommended by NEMA. However, if the owner of the transformer decides to handle the disposal of the unit himself, the unit is shipped back to the owner. Disposal is then usually made through a local junk dealer.

3.2.2.2 Repair of Failed Transformers

In talking with a major transformer manufacturing company which specializes in the servicing of transformers, it was learned that PCBs used by service shops are primarily for refilling the units which have failed and have to be repaired. Apparently, very few facilities handle their own servicing. Major service work is almost always handled by repair shops while minor service work, such as changing a gasket, to prevent a minor leak, may be taken care of by the owner of the transformer. Additionally, the repair

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shops often handle askarel conditioning services. In such a case, the serviceman carries the filter press to the customer's site and performs this service on site. Several gallons of PCBs are used in this service for topping the unit and adjusting the level. The procedure for the repair or disposal of failed transformers and the handling of the PCB liquid in those transformers is summarized in Figures 3.2.2.2-1 and 3.2.2.2-2.

A number of potential sources of environmental contamination have been identified, and are discussed in detail in the following notes to the figures.

1) Testing and analysis of PCB transformer fluid has been largely discontinued due to the strict requirements imposed on the disposal of the samples. This change in procedure may be expected to increase the probability of major failures of transformers containing PCBs.

2) Accidental spills of PCBs from transformers can occur due to leaks, venting caused by short circuits, or mechanical damage to the transformer case. In most cases, the transformer is contained in a vault or is surrounded by dikes which will limit the spill to a controlled area. Only in the case of railroad transformers would the leakage resulting from an accident be expected to be uncontrolled.

3) Transformers which are scrapped by the owner/user may be a serious potential source of pollution. Those transformers built during the past several years are well marked with the hazards of the PCBs which they contain. Disposal of junked transformers by electrical repair shops is governed by a detailed specification of the National Electrical

MONS 052704

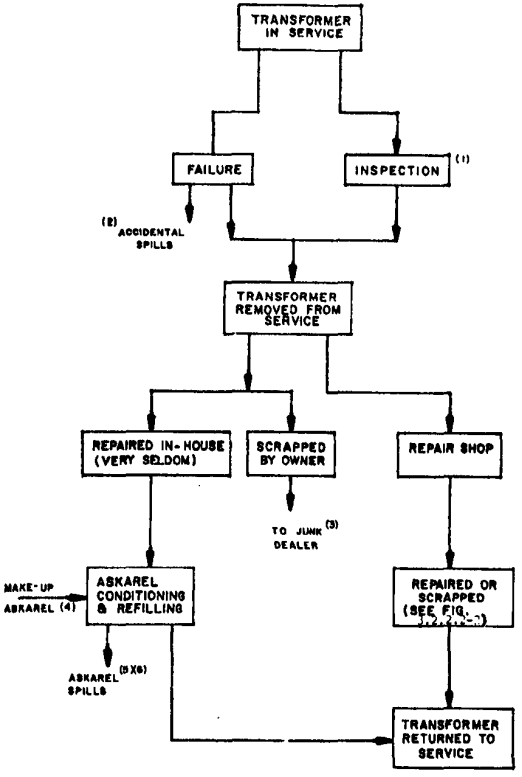

FIGURE 3.2.2.2-1. TRANSFORMER MAINTENANCE & SERVICING

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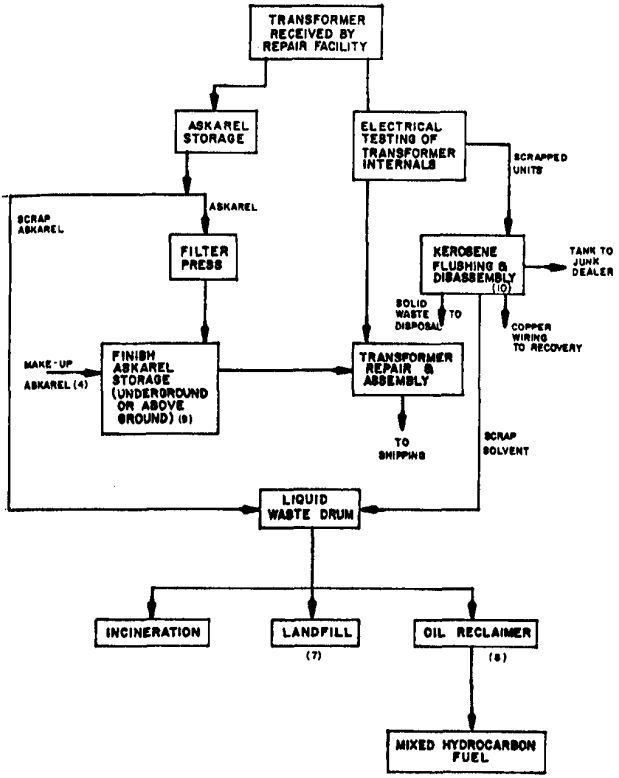

FIGURE 3.2.2.2-2. TRANSFORMER REPAIR

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Manufacturers Association (NEMA). However, the disposal of transformers through small local junk yards may result in significant pollution because:

a) The junk yards are not familiar with PCB handling procedures.

b) The older transformers are not marked with special instructions.

c) 90 to 95 percent of the transformers seen by the junk yards would contain mineral oil, and the occasional transformer containing PCB would be noted only as containing non-flammable transformer oil. This would not result in any special handling of the PCBs.

d) Disposal of PCBs by open burning in a trash incinerator will not completely destroy the PCBs, but will vaporize this material and disperse it into the atmosphere.

This is only a potential problem at this time, as uncontrolled scrapping of transformers has not been documented. However, several responses to the questionnaire claimed that uncontrolled handling of PCB filled transformers by junk yards was thought to have occurred in the past.

4) Considerable PCB is shipped in 55 gallon drums to repair shops and users. The residue in each drum after it is emptied may contain up to a pound of PCB. Empty drums which are recycled to drum reclaiming facilities or scrap yards would introduce this relatively small, but significant, amount of PCB into an uncontrolled environment. All drums presently in use have detailed handling instructions painted on the drum, and this information

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should minimize any potential problems from this source.

5) Filter residues and losses are in general treated as any other waste containing PCBs and are being placed in drums and held for controlled disposal.

6) Scrap PCB is packaged in 55 gallon drums. The NEMA instructions are very specific as to the required disposal procedures for this material. Small repair shops which do not have access to controlled disposal sites or services have been known to mishandle the scrap PCB by disposing into uncontrolled landfills (note 7) or through oil recovery services (note 8).

7) Landfills are a satisfactory disposal method for scrap PCB transformer oil if the leach water is monitored. In a few cases scrap PCB and PCB contaminated material is sent to a municipal dump.

8) At least one case is suspected where PCB transformer oil may have been sent to an oil reclaiming company which mixed it with other hydrocarbon wastes and sold it to a power company as fuel. It should be noted that the mineral oil used in 90 to 95 percent of the transformers presently in service. Problems may result when PCB transformer oils are mixed with mineral oils and handled in this manner.

9) New and conditioned PCB transformer oil is normally stored in large surface or underground tanks at the repair shop. Leakage may occur from

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these tanks into ground waters. No standards have been established for checking for such losses.

10) The scrapping of unrepairable transformers is covered by the NEMA standard (ANSI C107.1-1974). This standard requires that the transformer be drained and then flushed with solvent to remove PCB residues before the metal values are reclaimed. Possible sources of contamination would be incomplete flushing and the mixture of used solvent with hydrocarbon rather than with PCB residues. This is considered unlikely in the major transformer repair shops.

3.2.2.3 PCB Usage in the Transformer Repair Industry

The PCB usage figures for the transformer manufacturing and repair industries are summarized below.

	PCBs Use, lbs				
	1971	1972	1973	1974	1st half-1975
New PCBs used to repair transformers	590,000	580,000	440,000	780,000	480,000
PCB reclaimed and reused in repair of transformers	2,000	64,000	160,000	110,000	78,000
PCB shipped to user to replace transformer losses	3,000	3,000	4,000	2,000	2,000
PCB disposed in transformer repair				570,000*	
PCB used in transformer manufacturing				11,000,000	
Total PCB in service in transformers				270,000,000	

* This figure may include PCBs contaminated wastes as well as PCB.

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3.2.2.4 Transformer Service Life

There have been relatively few failures of PCB filled transformers, and statistically significant data is not available to support service life estimates. General estimates by transformer manufacturers indicate the following expected service life of this equipment:

Service life of substation transformers	40+ years
Service life of power transformers, including those on railroad locomotives	30 years

Transformers exhibit a small but significant infant mortality rate (failure within the first year of service). Overall transformer failure rate estimates are in the range of 0.2 percent per year.

3.2.2.5 Usage rate of PCBs in Transformer Repair

The total PCB used in 1974 in the repair of transformers was approximately 0.3 percent of the estimated total PCBs in service in transformers. This figure is consistent with the estimated failure rate of 0.2 percent per year for in-service transformers.

The usage of PCB in the transformer repair industry is approximately 7 percent of that of the transformer manufacturing industry.

3.3 Investment Casting

The investment casting industry produces precision-cast metal parts and shapes for the aircraft and other machinery manufacturing industries. Approximately 25 of the 135 investment casting foundries in the United States currently use PCB filled waxes in the manufacture of metal castings. The PCB incorporated in the waxes is decachlorobiphenyl (deka). The remaining foundries use either polychlorinated terphenyl (PCT) filled waxes or unfilled waxes. This section presents a review of the usage of deka filled waxes in the industry, including available information on use history, process technology, and potential

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PCB-bearing waste streams. Currently available information on PCTs usage in the industry is also included.

3.3.1 Background

There are currently 135 investment casting (IC) foundries and five investment casting wax manufacturing plants in the United States. The IC industry had its start in the United States during World War II when urgent demands for arms and aircraft parts required more efficient methods of producing finished, precision parts than standard machining techniques offered. During the war the waxes used by IC foundries consisted of a blend of carnauba wax, beeswax, paraffin, and rosins. However, over the last decade wax formulations have evolved which consist of a variety of polymeric compounds and other fillers such as decachlorobiphenyl and PCTs. By reducing the wax content through low-shrinkage fillers (such as PCBs and PCTs) volumetric shrinkage of the ceramic mold is controlled. This allows the production of metal castings with smaller dimensional tolerances than were available with the original unfilled waxes.

The major wax manufacturing companies are:

1. Yates Manufacturing Company, Inc.
2. M. Argueso and Company, Inc.
3. Freeman Manufacturing Company
4. J. F. McCoughlin Company

The Yates Manufacturing Company, Chicago, Ill., is the sole known U.S. supplier of deka waxes. The decachlorobiphenyl content is 30 percent of the total wax by weight (Solomon, P., Yates Manufacturing). Yates currently imports deka from Caffaro S.P.A., Italy, at a rate of 300,000 to 500,000 lbs. per year, which corresponds to the manufacture of between 1 and 1.5 million pounds of deka wax, annually. At a cost of $0.70 per pound, (Lewis, W.H., Signicast Corp.) the annual volume of sales of deka wax should be in the range of $700,000 to $1 million per year.

All the wax manufacturers listed previously are believed to use imported PCTs as pattern wax fillers. Since the general properties of the deka and PCTs are similar, it is believed that the wax production and use

MONS 052711

processes are similar also. Contacts with industry indicate that the volume of PCTs in wax is probably about the same as or greater than that of deka PCBs. Monsanto was the leading (and probably only) U.S. producer of PCTs prior to their voluntary cessation of production in 1972. Domestic production of PCTs by Monsanto through 1972 was as follows:

Year	Million of Pounds Aroclor 5460
1968	8.87
1969	11.60
1970	17.77
1971	20.21
1972	8.13

It is believed that a relatively small fraction of this production was used in casting waxes, probably on the order of a million or so pounds per year. Aroclor 5460 (Monsanto's trade name for their 60-percent-chlorine PCTs) was used primarily in adhesives, lubricants and paper coatings.

The current source of imported PCTs is believed to be Prodelec (France), which markets the material as Electrophenyl T-60 (60 percent chlorine), which, it should also be noted, may contain PCB contaminants.

In summary, the investment casting process, which is described more thoroughly in Sections 3.3.2.1 and 3.3.2.2, is a lost-wax casting process in which the shape to be cast is molded from wax and then invested or surrounded by a slurry of refractory ceramic. After the ceramic mold has hardened to an appropriate strength, the wax is melted or burned out leaving a molded cavity. Molten metal is then poured into the cavity, and cooled to form the casting.

The major losses of the virgin and used waxes occur during the dewaxing of the ceramic mold. As the ceramic mold is heated to remove the wax, a small portion of the wax diffuses into pores of the mold. Later, the mold with the trapped waxes is fired in a furnace to set the mold and remove the wax. Depending on furnace conditions, the decachlorobiphenyl in the wax may be burned or released to the atmosphere. At least several percent of that used is believed to be emitted via this route.

MONS 052712

It is a normal practice by many foundries to recover the drained pattern wax and reuse it several times in sprues and gates. Purchased wax is apparently used an average of 2.5 times. During the dewaxing process the virgin wax (used to form the pattern) and the old wax (used to form the gates and sprues) are collected as one mixture. Little of the wax is destroyed in the process; therefore, it is considered probable that the investment casting foundries store or dispose of relatively large amounts of used PCB-containing wax.

3.3.2 Investment Casting Technologies

3.3.2.1 Principles of Investment Casting

The principles of investment casting are the same for both the solid mold and shell processes, but the method of forming the ceramic mold differs somewhat between the two. Both require a pattern, gating to a central sprue, removal of the pattern by melting, pouring metal into the cavity left by the melted pattern, removal of mold material from the cast cluster, and cutting of castings from the sprue.

The investment shell process is depicted in Figure 3.3.2.1-1.

The Pattern: The process begins with production of a one piece heat-disposable pattern. This pattern is usually made by injecting wax or plastic into a metal die. Dies range from simple, hand-operated single-cavity tools to fully automated multi-cavity devices, depending on production quantities and complexity of the parts to be cast.

A heat-disposable pattern is required for each unit being cast. Each pattern has the exact geometry of the required finished part, but they are made slightly larger in order to compensate for volumetric shrinkage during the pattern production stage and during solidification of the metal in the mold.

The pattern carries one or more gates which are usually located at the heaviest casting section. The gate has three functions:

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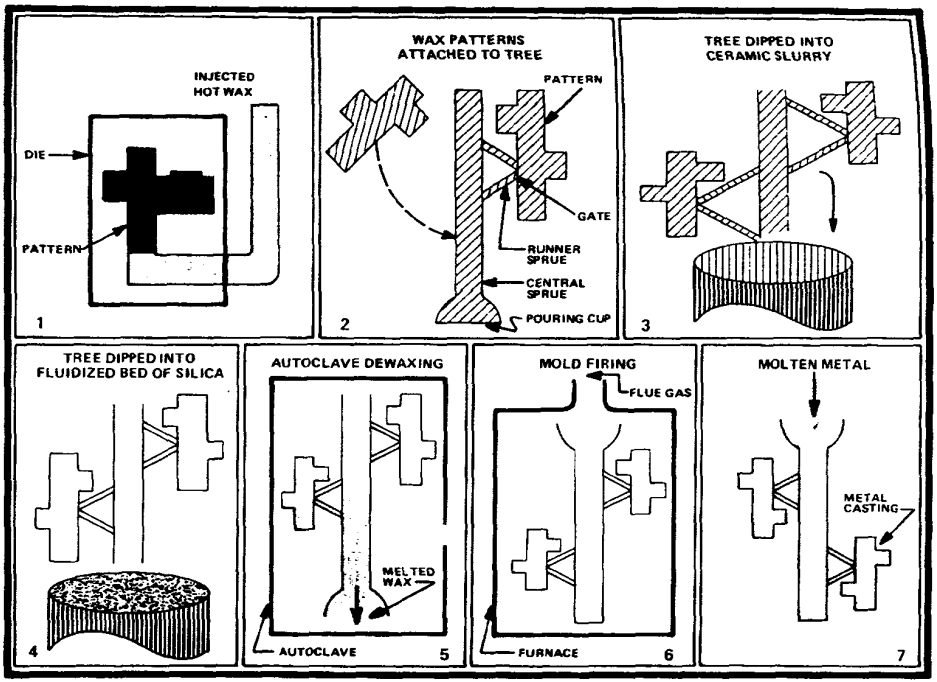

Figure 3.3.2.1-1. INVESTMENT SHELL PROCESS

(1) To attach patterns to the centrally-located sprue or runner, thus forming a tree-shaped cluster;

(2) To provide a passage for the draining of pattern wax once the mold is sufficiently hardened and has been heated; and

(3) To guide molten metal entering the mold cavity in the pouring operation.

Clustering: Patterns are fastened by the gate to one or more runners. The runners are attached to a pouring cup. All of these parts are usually made of wax. Patterns, runners and pouring cup comprise the cluster or tree upon which the ceramic mold is formed. The number of runners and their arrangement on the pouring cup may vary considerably, depending on alloy type and the size and configuration of the casting.

Molding: Up to the point of forming the ceramic mold, all foundries operate in essentially the same manner. After assembling the pattern to a tree, however, they may form the mold by either the investment flask process or the investment shell process.

Solid Mold or Investment Flask Process: There are two investment flask techniques, depending on the type of alloy to be poured. Ferrous alloys require highly refractory materials and binders. The entire cluster is dipped into a ceramic slurry, drained and stuccoed with fine ceramic sand. This step is usually repeated after the first coating has dried. This coated cluster is then placed in an open-end metal can (the flask) which is filled with a coarse slurry of ceramic backup material (investment). The investment hardens to comprise a green mold. When the flask with its contents are placed into an autoclave, the whole cluster (consisting of wax patterns, runners and sprues) melts and runs out through the pouring cup. The resulting monolithic mold contains cavities of the desired casting shape, with passages leading to them.

Nonferrous alloys are cast in ceramic molds bonded with plaster of paris. The entire tree (heat-disposable patterns, gates, runners, and pouring cup) is placed in an open-end metal flask without a first

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ceramic coating. Investment slurry is poured into the flask, completely surrounding the cluster. Before the binder sets up, the flask is placed under vacuum to remove all air entrapped during mixing of the investment. When the investment becomes hard, patterns are melted out exactly as in ferrous casting.

The Investment Shell Process: This technique, as described in Figure 3.3.2.1-1, involves dipping the entire cluster into a ceramic slurry, draining it, then coating it with fine ceramic sand. After drying, the process is repeated several times, using progressively coarser grades of ceramic material, until a self-supporting shell has been formed. The thickness of the shell is usually between 3/16 and 5/8 inch.

The coated cluster is then placed in a steam autoclave where the wax melts and runs out through the gates, runners, and pouring cup. The resulting ceramic shell contains cavities of the desired casting shape, with passages leading to them.

Casting: Monolithic shell molds and solid molds must be fired to burn out the last traces of pattern material and to attain a degree of permeability before the molds can be filled with metal. In the case of solid molds, this heating has to proceed slowly, in a controlled cycle which stretches over 12 to 18 hours, to avoid cracking of the mold. The shell molds, made of ceramic material with an extremely low coefficient of expansion, can be placed immediately into a hot furnace. Because the shell molds have relatively thin walls, they can be fired and ready to pour after only a few hours in the furnaces.

The hot molds may rely on gravity alone to carry the molten metal into the intricacies of the mold, as is common in sand casting, or the process may use vacuum, pressure and/or centrifugal force in order to faithfully reproduce intricate details of the wax patterns.

Melting equipment employed depends on the alloy. For nonferrous alloys, gas fired or electric crucible furnaces are usually used. For ferrous alloys, high frequency induction furnaces and indirect arc furnaces are common.

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Cleaning: After cooling, mold materials are removed from the casting cluster with vibrating equipment. Individual castings are usually removed from the cluster by means of cut-off wheels, and any remaining protrusions left by gates or runners are removed by belt-grinding. Generally, castings are sand blasted for smooth finish, then they are ready for such secondary operations as heat treating, straightening and machining.

Reclaiming of Pattern Waxes: The present cost of virgin pattern wax is approximately $.79/lb. In the future, it may be more economical to reclaim wax for use as pattern waxes, in addition to its present use in gates and runners. Furthermore, through a precipitation method, it is possible to remove fillers, including PCBs, from used wax in order to prepare unfilled wax.

Improvement of Investment Casting Processes: Several improvements in the investment casting techniques and procedures have been suggested by TRW Metals in Minerva, Ohio, which developed them through a two-year Air Force contract (AFML-TR-74-237). The areas of improvement were in wax pattern formation, mold production processes and metal pouring.

Wax pattern formation techniques were improved through simultaneous multiple injections of the gates and runners. The usual procedure requires separate steps.

Two suggestions for improvements were made for the mold production process: (1) elimination of the drying cycle between slurry dipping and sand coating, and (2) the use of microwave ovens to melt pattern wax out of the ceramic mold or shell.

The use of microwave dewaxers would have the advantage of reducing wax emissions in flue gas and drain condensates of autoclave ovens. However, microwave dewaxing may not eliminate wax losses occurring during mold firing as a result of wax trapped in the pores and cavities of the ceramic mold.

3.3.2.2 Foundry Process - Use of PCT and PCB Filled Waxes

A flow chart which typifies the use of PCBs and PCTs in investment casting is presented in Figure 3.3.2.2-1. PCB filled waxes are

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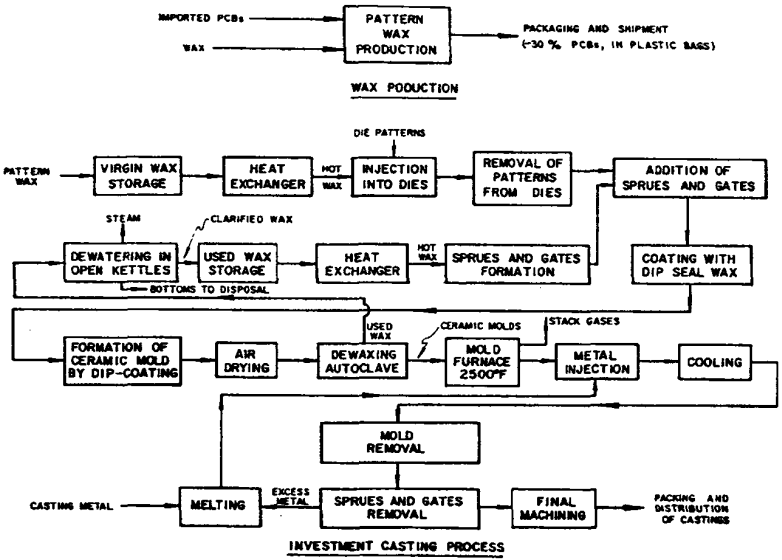

FIGURE 3.3.2.2-1
FLOW CHART OF PCBs USAGE IN INVESTMENT CASTING

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purchased from wax manufacturers in bulk quantities of 10,000 or more pounds, sealed in plastic bags and contained in boxes for shipment. The received pattern wax is stored in a stockroom at the foundry until melted for the production of wax patterns. Once melted, the wax is injected into a pattern die where the wax is allowed to solidify. The pattern die is then disassembled and the wax pattern removed. Several wax patterns are produced before forming the tree. The formation of the tree entails attaching the individual wax patterns to the sprues and gates, and after the trees are assembled, the sprues are coated with a dip-seal wax to fill the voids on the rough sprue surfaces.

The next step in the process is the formation of the ceramic mold. This is accomplished by dip-coating the wax trees in a ceramic slurry and a fluidized bed of silica, and air drying of the coated tree. This process is repeated several times before the wax is melted out of the mold.

Dewaxing is accomplished by one of three techniques: steam autoclave, microwave oven, or flash firing in a mold furnace. Most foundries apparently use the autoclave technique, which involves subjecting the ceramic coated trees to steam until the wax within the mold is melted out, leaving the ceramic shell. The melted wax is either disposed of or reclaimed for use as sprues and gate wax. The new microwave technique involves heating the molds with microwave energy. Microwave units of 5- and 10-kilowatt output are commercially available for this application. The third technique of flash firing combines dewaxing and mold firing in one step. The ceramic coated wax trees are placed in a furnace where all the wax is removed from the tree by flash firing. Most of the wax is vaporized and leaves the furnace with the stack gases. It is not known how many facilities use flash firing.

If the foundry dewaxes the trees using autoclave or microwave techniques, the dewaxed ceramic molds must be fired in the mold furnace to strengthen the ceramic and to remove wax residues. The ceramic molds are raised to temperatures of between 1900 and 2000°F for approximately two hours. The vaporized wax residues leave the furnace with the stack gases. The foundries claim that only 1 to 2 percent of the wax remains in the molds before mold firing. This estimate of trapped or wall absorbed wax appears to be low for two reasons:

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(1) The porosity of the ceramic mold can be as high as 30 percent, and

(2) Trapped waxes in the cavities of the pattern vary in amount, depending on the pattern's geometric configuration.

After firing, the ceramics are ready for metal pouring. The steps involved in pouring, and the subsequent recovery of the castings are evident in Figure 3.3.2.2-1, starting with metal pouring.

The high cost of pattern wax has stimulated foundries to reclaim used wax. For example, the PCB filled waxes sell for approximately 70 cents per pound. The average weight ratio between pattern wax and wax in sprues and gates is about 40:60. Therefore, reclaiming of used wax, especially for use in sprues and gates, ahs become a very important part of the foundry process.

Reclaiming involves placing the used wax in open kettles or tanks and heating it above the boiling point of water until all the water (from the steam autoclave) is eliminated. After dewatering, the reclaimed wax is reconstituted by adding paraffin and other additives until certain melting-point specifications are met. It is claimed that wax fillers are not added to adjust the filler content (Wurster, W., Consolidated Casting Corp.).

For those foundries which practice wax reclamation on their used wax, it is estimated that 5 to 10 percent of the wax is deliberately disposed of. The major source of the discarded wax is probably the dregs from the dewatering kettles.

3.3.2.3 Waste Streams

Idealized waste streams (containing PCBs and PCTs) leaving an investment casting foundry are shown in Figure 3.3.2.3-1. The broken lines within the process box in Figure 3.3.2.3-1 indicate potential PCB and PCT escape routes via air emissions from the foundry unit processes. The solid lines between the processes indicate the production routes of the waxes.

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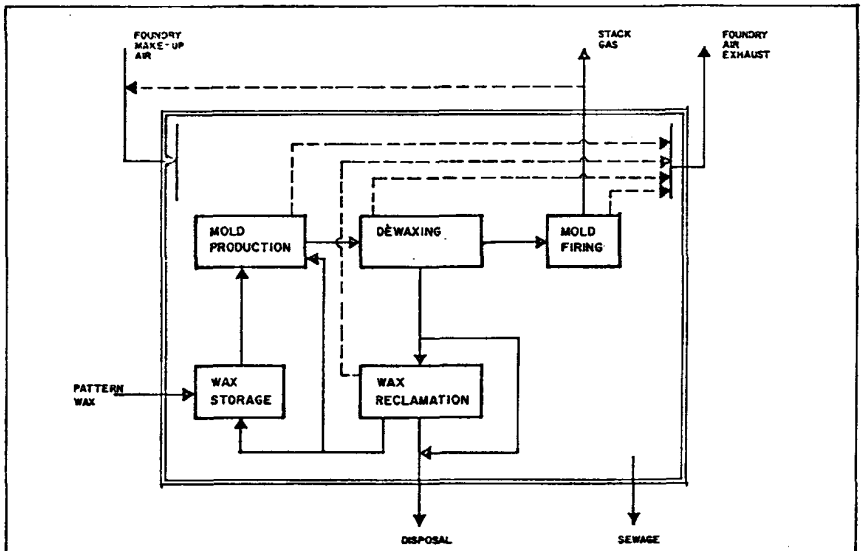

FIGURE 3.3.2.3-1

IDEALIZED FLOW CHART FOR AN INVESTMENT CASTING FOUNDRY, SHOWING WASTE STREAMS

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The solid lines at the top of the figure indicate the two general ambient air escape routes, namely the stack gas from the mold firing furnace and the foundry exhaust air system. The two solid lines leaving the foundry (at the bottom of the figure) represent PCB and PCT escape routes: solid waste, which is usually sent to landfills, and raw sewage, which goes to municipal sewage treatment in most cases. The broken line outside the facility (at the top of the figure) indicates the possibility for inadvertent recycling of escaped PCBs or PCTs in stack gas or foundry air exhaust back into the foundry facility.

PCB-PCT-containing waxes enter the foundry as pattern wax packaged in plastic lined boxes which are stored until needed in the casting process. During mold production, when the wax is melted and injected into metal dies, wax fumes may escape. The type of dewaxing method employed by the foundries has a direct effect on the amount and mode of PCB or PCT loss to the environment, not only during dewaxing but also during process steps that follow. For example, the use of a steam autoclave, in addition to its own potential emission of PCBs or OCTs, also imparts moisture to the wax, and this water must be removed before the wax can be reused. Dewatering by evaporation at high temperature also likely contributes to air emissions. Flash firing, which combines mold firing and dewaxing into one step, probably emits high levels of PCBs or PCTs, and so far as is known, emission controls are not used.

Solid wastes can include unreclaimed used wax, excess reclaimed wax, bottoms from reclamations, and wastes from spills, equipment cleanout, etc. Although process water does not appear to be used, some plants may use cooling water. The steam autoclave appears to be a source of water vapor only.

3.3.3 Wax Manufacturing

To date, very little is known about the wax manufacturing process. However, it is known that in the process PCB or PCT compounds are added in powdered form to the wax base. Reduction of PCB or PCT particle size prior to mixing may be desired. Losses of dust to the environment by air routes from both size reduction and mixing operations would be expected.

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3.3.4 Recommendations

The information presented herein represents the current knowledge of decachlorobiphenyl and polychlorinated terphenyls usage as wax fillers in the investment casting industry. This knowledge should be used as a basis for the development of an accurate assessment of the importance of PCB and PCT waste from the industry, and of the adequacy of available substitutes. Significant information gathering efforts would be required to establish a complete picture of the practices, processes and product of the investment casting foundries and wax manufacturers. Definition of the waste streams and emissions from the processes used would require sampling and analysis efforts in addition to the gathering of available process data and other information from the industry. The objectives of such a plan would necessarily include the following:

(1) Verification of the magnitude of PCB and PCT wax filler production and use;

(2) Development of detailed process descriptions, including waste streams, leading to a complete mass balance for the production and use processes (including significant variations);

(3) Definition of quantities and concentrations of waste streams, including waste form, abatement techniques, and ultimate disposal methods; and

(4) Evaluation of all reasonable alternatives to the use of PCBs and PCTs in casting.

A study plan to accomplish the above objectives was developed for OTS under Task III of this program (Contract 68-01-3259).

3.4 Secondary Fiber Recovery (Paper Recycling)

The secondary fiber recovery industry converts wastepaper from industrial, commercial, and municipal sources into reusable pulp, which is subsequently used to produce paper products, either as is or blended with virgin pulp. In the United States, there are approximately 230 paper mills

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which produce pulp completely derived from wastepaper and 550 mills whose generated pulp contains secondary fiber (typically 10 to 15 percent).

Wastepaper stands third behind pulpwood and wastes from other forest products as a source of paper pulp in the United States. In 1974, fiber recovery mills removed almost 13 million tons of wastepaper from the nation's solid waste streams.

The effluent discharges from some of the secondary fiber mills has been documented by Kleinert to contain Aroclor 1242,[1] an apparent incidental PCB contaminant occurring in the pulp production process. Table 3.4-1 shows the PCB (as Aroclor 1242) concentrations and discharge rates for some paper recovery within the State of Wisconsin. These data were collected in 1975 by the Wisconsin Department of Natural Resources in an effort to survey PCB discharges.

The following subsections present a review of the historical usage of Aroclor 1242 in carbonless copy paper production and a brief description of a secondary fiber recovery process.

3.4.1 Historical Use of PCBs in the Paper Industry

Aroclor 1242 (which appears to be the predominant PCB found in mill effluents)[1] was used in the manufacture of carbonless copy paper sold by the Appleton Paper Division of the NCR Corporation during the period 1957 to 1971. Tables 3.4.1-1 through 3.4.1-3 provide data indicating: (1) The magnitude of Aroclor 1242 consumption in the manufacture of NCR carbonless paper; (2) Production quantities of NCR carbonless paper; and (3) The weight percent of Aroclor 1242 in carbonless paper.

From these tables, several significant facts are derived concerning the magnitude of PCB use in the manufacture of carbonless paper products. Some of these facts are:

(1) Approximately 44 million pounds of Aroclor 1242 were purchased (from Monsanto) for the manufacture of NCR carbonless paper;

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TABLE 3.4-1

PCB CONCENTRATIONS IN WISCONSIN PAPER PLANT EFFLUENTS

Plant	No. of Determinations	Average PCB Concentration (ppb)	PCB Discharged lbs./day	Aroclor Type
Badger Paper Mills	1	<.1	-	
Scott Paper				
Marinette	1	<.1	-	
Oconto Falls	1	<.1	-	
Shawano Paper	1	<.1	-	
John Strange Paper	1	4.00	.037	1242
Bergstrom Paper	4	28.40	1.25	1242
Kimberly Clark	1	0.28	.010	1242
Thilmany Paper	2	<.1	-	
Fort Howard Paper				
Mill Effluent	1	2.60	0.158	1242
Deinking	1	6.40	0.586	1242
Deinking & Mill Effluent	3	7.07	1.060	1242
American Can				
Sulfite Sewer	1	0.10	0.002	1242
Paper Mill Lagoon	1	0.14	.012	1242
Charmin Paper	1	0.14	.019	1242
Green Bay Packaging	1	0.45	0.006	1242

Note: Effluent flow data for these companies was determined at time of PCB sampling.

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TABLE 3.4.1-1

HISTORY OF AROCLOR 1242 CONSUMPTION
IN THE MANUFACTURE OF NCR CARBONLESS PAPER
FOR THE YEARS 1957 THROUGH 1971[1]

YEAR	(THOUSANDS OF POUNDS)
1957	587
1958	779
1959	1019
1960	1149
1961	1643
1962	1953
1963	2281
1964	2705
1965	3489
1966	4246
1967	4355
1968	5801
1969	6278
1970	6611
1971	1266
TOTAL - 1957 through 1971	44162

Note: [1] From data compiled and reported by Appleton Papers Division, NCR Corporation.

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TABLE 3.4.1-2

HISTORY OF NCR CARBONLESS PAPER PRODUCTION
FOR THE YEARS 1957 THROUGH 1971

YEAR	ESTIMATED NCR CARBONLESS PAPER PRODUCTION - TONS
1957	10010
1958	13264
1959	17434
1960	20703
1961	25504
1962	29708
1963	34583
1964	41762
1965	51855
1966	60594
1967	69512
1968	83250
1969	87336
1970	91576
1971	88977
TOTAL,[1] 1957 through 1970	726068

Note: [1] Total excludes 1971 because use of Aroclor 1242 was discontinued in May, 1971 but estimated production of NCR carbonless paper is for full year.

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TABLE 3.4.1-3

RATIO OF AROCLOR 1242 CONSUMPTION FOR CARBONLESS TO NCR CARBONLESS ESTIMATED PRODUCTION

Year	(A) Aroclor 1242 Consumption Thousands of Pounds (1)	(B) NCR Carbonless Estimated Production Thousands of Pounds	PCB Content $\frac{(A)}{(B)} \times 100$
1957	587	20020	2.9
1958	779	26528	2.9
1959	1019	34868	2.9
1960	1149	41406	2.8
1961	1643	51008	3.2
1962	1953	59416	3.3
1963	2281	69166	3.3
1964	2705	83524	3.2
1965	3489	103710	3.4
1966	4246	121188	3.5
1967	4355	139024	3.1
1968	5801	166500	3.5
1969	6278	174672	3.6
1970	6611	183152	3.6
1971	1266	177954	-
TOTAL (2) 1957 thru 1970	42896	1274182	Avg. 3.4%

Notes: (1) From data compiled and reported by Appleton Papers Division, NCR Corporation.

(2) Total excludes 1971 because use of Aroclor 1242 was discontinued in May, 1971 but estimated production of NCR carbonless paper is for full year.

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(2) The average weight percent of Aroclor 1242 in carbonless paper was 3.4 percent;

(3) Of the total PCBs sold in the United States during 1957-1971, 6.3 percent were sold for the NCR carbonless paper application; and

(4) 28 percent of the total Aroclor 1242 sold by Monsanto for plasticizer applications was purchased for the manufacture of NCR carbonless paper.

Although NCR developed and sold the product, the actual manufacturing step whereby Aroclor 1242 was incorporated into the paper was performed by the Mead Corporation of Dayton, Ohio, who exclusively supplied carbonless paper to NCR. NCR, in turn, either used the supplied paper to manufacture ledger (business) forms or sold and distributed the carbonless paper to other form manufacturers. Aroclor 1242 is reported to be the only Aroclor type used in the production of carbonless paper. Specifically, Aroclor 1242 was used as a solvent for certain color reactants which were encapsulated into microspheres 10-20 microns in diameter and applied to one side of the paper during the coating process. The walls of the microspheres consisted of a gelatin-gum arobic formulation which was hardened by treatment with an aldehyde (such as formaldehyde). Since 1971, alkyl biphenyl compounds have been used in place of Aroclor 1242 as the dye carrier.

Very little is known about other uses of PCBs in the paper industry. Past usage of PCBs in paper coatings and adhesives appears likely, although the quantities used could not have been near the magnitude of PCB usage in the carbonless copy paper. Almost certainly PCBs were used in some of the inks, and possibly paper colorants, which can also be expected to occur in wastepaper. According to Monsanto, the favored Aroclor type used in inks was 1254, which contains most of the same isomers as 1242 but at different relative concentrations.

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In addition, PCBs can enter the pulping process through contamination of intake water and in virgin pulp. Little is known about the magnitude of any of these sources, or even how much carbonless copy paper containing PCBs remains in files, etc. to enter the paper recycling processes in the future.

3.4.2 Fiber Recovery Mill Process

The following is a generalized description of the mill process for recovering paper fiber. Portions of this description was provided by the Bergstrom Paper Company in Neenah, Wisconsin. Figure 3.4.2-1 depicts the general process, up to the paper making section, in block form.

The fiber recovery process is a purification process wherein fibrous materials are deinked and separated from non-fibrous materials through controlled cleaning and mechanical treatment, followed by washing and cleaning. The color is next removed from the pulp by a multi-stage bleaching system accompanied by intermittent washing and centrifugal dewatering.

Pulping and Deinking: The fiber regeneration process starts with feeder crews loading the sorted paper onto a belt conveyor. The conveyor feeds a hydropulper, where wastepaper is pulped and deinked through the action of hot water, steam, caustic soda, and deinking chemicals. The breaking down of the paper stock is accomplished through a combination of mechanical and chemical treatment. At this point, larger metallic objects and other non-paper materials mixed with the wastepaper are collected into traps at the bottom of the pulper. The pulped stock leaves the hydropulper via extrusion through perforated plates, and goes to blending chests for additional retention time and agitation. From the blending chests the stock passes over a vacuum filter which is used for heat and chemical recovery. Much of the filtrate is recycled to the hydropulper; excess filtrate goes to treatment. The stock is then diluted and sent to centrifflers where small metallic particles such as pins and staples are removed.

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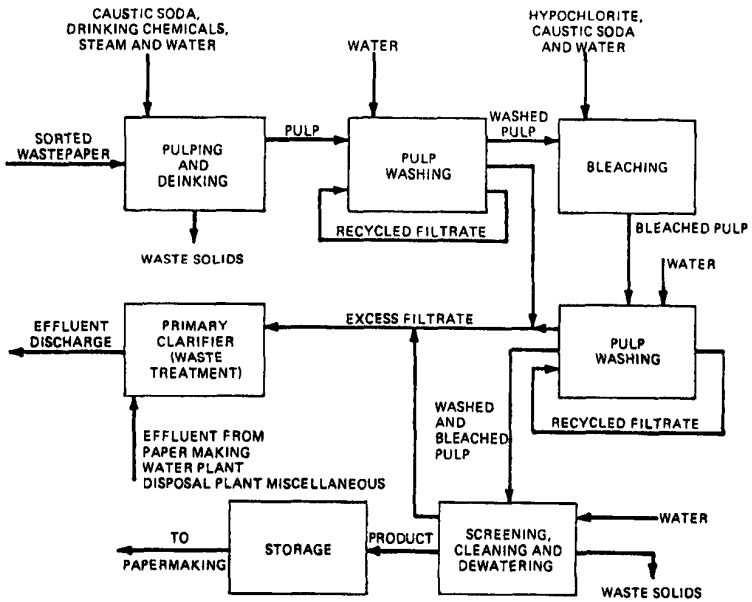

Figure 3.4.2-1. MILL FIBER RECOVERY PROCESS AND WATER EFFLUENTS

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Pulpwashing: Accepted stock from the centrifflers goes on to the washing stage. Stock washing is accomplished in a four-stage counter-flow washing system. The first stage consists of cylinder washing, the second and third stages consist of sidehill washers, and the fourth stage is another cylinder washer. The cleanest water is used for dilution at the fourth stage, and the filtrate is fed to the preceding stage, finally reaching the first stage from which the filtrate is discharged for waste treatment.

Bleaching: Following washing, the stock goes to a three-stage bleachery. At the first stage the stock is chlorinated by sodium hypochlorite solution in a tower. After chlorination, the stock is washed on a vacuum filter. In the next stage the stock is treated with caustic soda and sodium hypochlorite. After retention in a second tower the stock is diluted and again washed on a vacuum filter. It is then treated again with sodium hypochlorite in a third tower.

Screening and Cleaning: After retention in the third tower, the bleached stock is diluted for the next cleaning process, which is a three-stage pressure screen system. Accepted stock from the first stage pressure screen goes to a five-stage centrifugal cleaner system for removal of small-sized heavy contaminants. Following this, the pulp is sent to a four-stage system of centrifugal cleaners for removal of lightweight contaminants.

After the cleaning, the stock goes to a final washing stage and is then dewatered (thickened) and stored in high density towers for paper making.

Flow Rates and Composition of Discharges: At Bergstrom the separate waterborne discharges from the paper and the paper making process are combined with other facility waste streams and directed to a central waste treatment system. Only the effluent from the primary clarifier of the waste treatment system is discharged to the environment. The average effluent flow rate for Bergstrom during 1975 was 3.9 million gallons per day. This volume rate is broken down as follows:

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Process	Volume Rate to Waste Treatment Million Gallons/Day
Deinking	2.5
Paper Making	.9
Water Plant	.3
Disposal Plant and Miscellaneous	.2

Table 3.4.2-1 is a tabulation supplied by Bergstrom of the 1974 averages for various parameters in their raw water source and waste clarifier effluent. The average Aroclor 1242 concentration in the effluent was reported to be less than 8 ppb.

Recommendation (Paper Recycling): The information presented herein with regard to PCBs in paper recycling processes is based on a very limited study effort on the secondary fiber recovery industry. It is recommended that a more detailed study be performed of PCBs involvement in this industry. Important aspects which should be addressed include:

(1) Definition of paper recycling processes and the PCBs material balance therein (PCBs input versus PCBs content in effluent and product);

(2) Definition of past PCBs usage in paper and routes into recycled paper;

(3) Development of present distribution of PCBs originally used in paper;

(4) Determination of applicable effluent treatment methodology and associated cost estimates; and

(5) Projecting future contribution of PCBs to the environment from this industry.

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TABLE 3.4.2-1

COMPOSITION OF RAW WATER AND CLARIFIER EFFLUENT (1974 DATA)
(Bergstrom Paper Co.)

	Raw Water	Clarifier Effluent
Aldrin, µg/l	<0.1	<0.4
Ammonia Nitrogen, mg/l	0.32	1.72
Arsenic, µg/l	<8	<8
Barium, µg/l	14	140
Beryllium, µg/l	<0.3	<5
Boron, µg/l	33	235
Cadmium, µg/l	<16	<16
Chloride, mg/l	10	482
Chlorine, mg/l	<0.5	<0.5
Chromium, µg/l	<4	26
Cobalt, µg/l	<14	14
Copper, µg/l	<5	78
Cyanide, mg/l	<0.005	0.12
Dieldrin, µg/l	<0.03	<0.03
Fecal Coliform Count/100 ml	4	<10
Fluoride, mg/l	0.46	0.48
Heptachlor, µg/l	<0.07	<0.5
Lead, µg/l	<42	85
Manganese, µg/l	10	50
Mercury, µg/l	0.7	0.5
Nickel, µg/l	<33	<33
Nitrate Nitrogen, mg/l	0.29	1.32
Nitrite Nitrogen, mg/l	<0.005	0.43
Kjeldahl Nitrogen, mg/l	0.82	19.0
Oils, Fats, Grease, mg/l	<1	26.4
Phenol, µg/l	4	26
Phosphorus, mg/l	0.11	0.57
PCBs, µg/l	<0.5	8.0 (1242)
Selenium, µg/l	<8	<8
Sulfate, mg/l	45	74
Sulfide, mg/l	<0.05	<0.05
Sulfite, mg/l	<2	<2
Suspended Solids, mg/l	<1	465
Thallium, µg/l	<1	<25
Zinc, µg/l	67	420
BOD_5, mg/l	1.1	665

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3.5 Industrial Use of PCBs as Hydraulic and Heat Transfer Fluids

3.5.1 General

The use of PCBs in hydraulic and heat transfer systems increased rapidly during the 1950s and 1960s until, in 1970, the maximum sales by Monsanto for these uses, plus lubricants, were about 11.3 million pounds, or over 15 percent of the total 1970 reported domestic sales. Since 1971, Monsanto has not marketed PCBs for these uses, and although it should be noted that such usage of PCBs in deep mining equipment is expressly allowed by the OECD agreement to which the U.S. is party.

When PCBs sales for heat transfer and hydraulic uses were eliminated by Monsanto in 1971, the affected industries turned to substitutes or, in a very few cases, imported PCBs. Phosphate esters have found acceptance in many types of hydraulic systems where PCBs were formerly used. Glycols and other alcohols have replaced PCBs in some heat transfer systems, and there are a number of other substitutes used for this purpose (including other chlorinated hydrocarbons).

It is surmised that there are industrial concerns still using PCBs in these semi-closed systems. Hesse reported at the National Conference on PCBs in November, 1975 that a number of such users had been found in Michigan. Later contacts with these same firms indicated that all had voluntarily replaced the PCBs in their systems with substitute fluids. Very little work has been done to ascertain the magnitude of current PCBs usage for hydraulic and heat transfer purposes. Of the total reported Monsanto domestic sales of PCBs over the period 1957-71 for heat transfer fluids, hydraulic fluids, and lubricants, 81 million pounds, it seems reasonable that at least 95 percent have been replaced by substitutes or were in systems now obsolete. On this basis the maximum amount still in use would be on the order of four million pounds. A figure of two million pounds still in use is probably more accurate.

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3.5.2 Use of Imported PCBs by Joy Manufacturing

Until recently, Joy Manufacturing Co. (Pittsburgh, Pa.) manufactured mining equipment which utilized a PCB motor coolant. Joy imports PCBs, as a mixture similar to Aroclor 1242, from France (Prodelec). Presently, the PCB type motors are no longer manufactured and have been replaced on new units by an air-cooled motor. However, PCB coolant fluids purchased from France are being used for servicing the old liquid coolant motors. Currently, there are approximately 1100 of the old motors in the field, each of which contains an estimated 3 - 4 gallons of PCB type coolant fluid. The operating time of these motors before complete overhaul is between 1 and 2 years. The major benefit derived from using the PCB type coolant was its fire retardant characteristics.

From the information received by representatives of Joy Manufacturing Company, and from available physical properties, it is estimated that between 40,000 and 60,000 pounds of the imported PCB type coolant fluid would be necessary to replace and "top off" the fluids in the old motors each year.

3.6 Recent Use of PCBs in Product Development Activities

Since the voluntary limitation on the sale of PCB compounds in the United States by Monsanto, small quantities of PCB compounds have been imported for new product development by at least one U.S. company. Such a use application, by E. I. duPont de Nemours and Co., Wilmington, Del., was for development work on a new polymer which is derived from the reaction of decachlorobiphenyl (deka) and Bisphenol A.

According to duPont representatives, they have imported small quantities of deka from Caffaro (Italy) for experimental purposes with the intent to develop a new product called NR-140 polymer. Approximately 2000 pounds of deka were imported in 1974; however, duPont did not import any deka in 1975. A decision was made not to commercialize the new product because of the uncertainties associated with the regulation of PCBs.

It is estimated by duPont that, if the new product had been commercialized, the annual purchase of deka would be in the range of 5-10 million pounds.

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SECTION VI

WASTE TREATMENT TECHNOLOGIES

1.0 INTRODUCTION

This section includes descriptions and discussions of existing and proposed technologies for the treatment of various types of wastes generated at PCB-producing and PCB-using plants. Also included are discussions of the presently available control technologies and technologies to be available within three years, plus technologies that will not be available for five or more years. The treatment and control costs included here have been developed and presented in the Task II report "Assessment of Wastewater Management, Treatment Technology, and Associated Costs for Abatement of PCBs Concentrations in Industrial Effluents", EPA Contract No. 68-01-3259, issued February 3, 1976.

1.1 Summary of Waste Management Problem Areas

Based upon detailed plant inspections and examinations of the processes in the production of PCBs and their use in capacitors and transformers, it has been determined that there are four major categories of wastes to be considered: waste liquid PCBs, PCBs in wastewater, PCB contaminated solid wastes, and airborne PCB emissions. It has also been determined that the characteristics of wastes in PCBs producing and using operations are similar enough that the same kinds of control and treatment technologies can be used.

1.1.1 Waste Liquid PCBs and Contaminated Scrap Oil

The users of dielectric materials have strict requirements for purity. Typical requirements are:

Inorganic chlorides	100 ppb maximum
Acidity, mg KOH/g	0.01 maximum
Water content	30 to 35 ppm maximum
Resistivity, 100°C, 500 V, 0.1 inch gap	100 to 500 x 10^9 ohm-cm, minimum
Dielectric strength, 25°C	35 kv minimum

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When these or other properties cannot be met at the producer's facility, or by the user during transformer and capacitor filling operations, and it is found that the properties cannot be restored to askarel specifications by filtering and drying, disposal is required. The types of PCB contaminated liquids requiring disposal are:

1. PCBs contaminated with mineral oil
2. Mineral oil contaminated with PCBs
3. Nonreclaimable contaminated transformer askarels - arced askarels, askarels from manufacturing spills and sump accumulations, and askarels from holding basins, drip and drain pans, washings, sample jars and containers

1.1.2 PCBs in Wastewaters

The most likely pathways by which PCBs enter wastewater streams are operator wash-up after PCB handling and groundspills that mix into rainwater runoff. The significance of the first pathway can be illustrated by the realization that sixteen operators (or 4 operators 4 times a day) washing 1 ounce per day of PCB from their hands, account for one pound per day of PCB discharge.

Other wastewater categories discussed in the industrial characterization section of this report are:

1. Incinerator scrubber and quench water
2. Steam jet ejectors in vacuum distillation
3. Capacitor detergent wash solutions

1.1.3 PCB-Contaminated Solid Wastes

Solid wastes can be divided into two categories, burnable and nonburnable.

1.1.3.1 Burnable Solid Waste Materials Containing PCBs

Burnable wastes can be disposed of by high-temperature incineration. Such wastes consist of cellulosic materials, rags, pressboard, wood, sawdust, fuller's earth in bulk or in cloth bags, blotter papers, nitrile or cork gaskets, and similar materials.

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1.1.3.2 Nonburnable Solid Waste Materials Containing, or Contaminated with PCBs

Nonburnable wastes may consist of capacitor and transformer internal components; steel, copper and aluminum components; filter units of the steel mesh construction type; and askarel drums and cans. Wastes of this type should be drained, with the liquid collected in drip pans, before disposal.

1.1.4 Air Emissions of PCBs

Although PCBs have very low vapor pressures they can be emitted to the atmosphere from the following operations and practices:

1. Aroclor scrubbing of air in PCBs manufacture
2. Vapor exhaust from steam jet ejectors
3. Evaporation from accidental spills
4. Evaporation from hot surfaces as part of flood-filling, inspection or holding operations
5. Vacuum pump exhausts
6. Evaporation from plant wastewater

1.2 Summary of Current PCBs Waste Control Practices

1.2.1 Control of Waste Liquid PCBs and Contaminated Scrap Oils

Plant visits have shown the major control methods to be incineration and disposal in sealed drums sent to sanitary landfills. Both incineration and landfilling may be carried out by the facility generating the waste, or the facility may engage a contractor.

Monsanto, the only U.S. producer of PCBs, has an incinerator (designed by John Zinc, Inc.) that vaporizes PCB liquids and sustains them in a turbulent burning gas at more than 2200°F for 2 seconds. One transformer manufacturer uses a John Zink designed incinerator that vaporizes PCBs and burns them at 1600 to 1800°F for 3 seconds or longer; this facility can also destroy PCBs soaked into transformer internal parts, but cannot routinely handle spent fuller's earth.

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A number of PCB users send their solid wastes to the Rollins Environmental Services facility at Logan Township, N.J. Rollins uses a specially designed complex having a rotary kiln and a liquid turbulent burning chamber, both of which exhaust into an afterburner. Liquids can be burned in either the liquid chamber or the kiln; in the kiln liquid wastes can help to incinerate solids. The afterburner is 40 feet long, providing good residence time, and it is followed by a hot duct of about equal length that allows further combustion. Rollins claims a residence time of 3 to 4 seconds at a minimum temperature of about 2400°F at the aft end of the hot duct. The gases then go to a venturi scrubber and a tower scrubber for cooling and neutralization. For non-PCB incineration, Rollins sometimes lowers combustion temperature to 2200°F and residence time to 2 to 3 seconds. These residence times and temperatures were chosen experimentally to get 99.999-percent PCB destruction. This facility also handles all kinds of solids, as will be explained later, and it operates with EPA approval.

Another facility that incinerates liquid PCBs, with New York State EPA approval, is the Chemtrol Corp.'s facility at Model City, New York.

Liquids going to landfill are sealed in drums and added to landfills that have deep clay bases and impervious bulkheads to prevent leaching and seepage. However, incineration is the preferred disposal method for liquids.

1.2.2 Control of PCBs in Wastewaters

Our plant investigations have revealed that there are no methods being practiced whereby dissolved or otherwise bound PCBs in water streams are being either extracted from those streams or destroyed in them.

In the separation of PCBs from wastewaters, PCBs and sludges are removed from the bottom of water bodies, while oily phases are removed from the surfaces. However, nothing as yet is being done to treat the water layer itself; this is the area of PCB wastes control and treatment most needing development.

In general, waste streams contain between 1 ppb and 500 ppb of PCBs; most levels range between 10 and 50 ppb. PCB concentration of less than 1 ppb are undetectable.

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Several plants use methods to keep the quantity of PCB contaminated wastewaters as small as possible. A few plants planned adsorption tests with carbons and other adsorbents, but there were no full-scale operations.

1.2.3 Control of Solid Wastes Contaminated with PCBs

The two current methods of disposal of solid or semi-solid PCBs wastes are incineration and landfill. Since we found only one PCB-using manufacturing facility with partial incineration capability, and Monsanto's incinerator cannot handle solids, all facilities except one must ship their solid wastes away from the plant site for either treatment. The one plant with partial capability can incinerate transformer internals to recover copper, and also can incinerate paper, rags, cardboard and the like. However, they do not as yet, incinerate fuller's earth, contaminated dirt, and similar materials. These are drummed and stored for later disposition.

Although there are a number of experimental facilities throughout the U.S. that could undboutedly incinerate all types of solid materials, one commercial venture has received the bulk of the work. Rollins Environmental Services can handle liquids incineration. For solids incineration of almost all types, the tumble burner or rotary kiln is used. When PCB contaminated materials are to be destroyed, the kiln temperature is brought up to 2200°F. All kinds of solids, packed in 47-gallon lined fiber drums and not posing unusual safety hazards are accepted. The current (late 1975) fee is about 7-1/2¢/pound. Additional charges of $3/fiber-drum handling, plus transportation charges, and possibly other charges for unusual problems, might be made.

Rollins will not accept impact sensitive, radioactive materials, or heavy metals concentrations of more than 25 ppm in the PCBs wastes. For wastes packed in steel drums, Rollins charges a $10/drum handling charge. As a general rule, anything packed according to the latest ICC tariff for hazardous materials will be accepted.

As with the liquids incineration, the gases from the kiln at 2200°F pass to the afterburner at a temperature of about 2500°F. Gases exit

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the afterburner to a long hot duct that completes combustion and maintains the temperature at 2400°F until the gases enter the venturi scrubber, and thence to the lower scrubber and then the stack. Rollins has experimented with lower temperatures of 2000 to 2200°F and has not found destruction of PCBs to be at the 99.999 percent level desired. The residence time for gases at the 2400°F must be 3 to 4 seconds in a turbulent regime.

With regard to landfilling, one commercial venture has handled a large quantity of the PCB solid wastes under supervised conditions. The Chemtrol Pollution Services Co. of Model City, N.Y., operates a landfill located on the shore of Lake Ontario, under New York State EPA supervision, in a geologic setting claimed to be ideal for complete containment.

This "scientific landfill" is located entirely above ground on a bed of 40-feet-thick clay. Constructed on this foundation are cells for receipt of drummed solid wastes. The cells are lined with 30-mil chlorinated polyethylene film, and when loaded, are sealed, or covered with 5-feet of clay. At the bottom of each cell there is a sump, so that all leachate is collected and removed. That leachate is pH controlled, settled, filtered, and treated by flow through a carbon bed. The ground and surface waters are checked monthly for chemical content by an outside analytical laboratory. The facility has been approved for usage as a PCB disposal site by the New York State EPA, and thousands of drums have been landfilled over the last five years. An inventory is kept of the contents of each cell.

Chemtrol has the capability of converting semisolids and sludges to solids by using silicate cement powders and proprietary gelling agents.

Our review and analysis of the industrial situation for PCBs solid wastes control shows there are adequate options, at higher prices, for safe disposal and destruction. There is no longer a justification for open dumping to the ground or in lagoons.

1.2.4 Control of Air Emissions of PCBs

Most air emissions from ambient temperature PCBs are not controlled or collected for treatment in any way. PCB emissions generally are

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collected as part of the overall plant air exhaust, which frequently is ducted to roof exhausts without treatment. Several plants used exhaust chilling and/or fibrous or granular filtration of air; these methods offer the potential for PCB emission reduction.

The hot flood-filling of capacitors is followed by a cool down period before the filling tank is opened to the plant atmosphere. However, the temperature is still between 100 and 150°F; the area of the opening is several square meters, through which tank gases can reach the plant atmosphere. The tanks have individual exhaust ducts, but they lead directly to a roof exhaust system. The PCB-covered capacitors are held in an oven at 100 to 150°F to prevent any moisture condensation before sealing. Vapors from this storage are ducted to the roof and vented also.

In some cases, waste scrap oils containing PCBs are burned together with fuel oil in standard boiler systems. In these instances much of the PCB content is probably vaporized and exhausted to the air, rather than incinerated.

2.0 CANDIDATE PCBs WASTE TREATMENT TECHNOLOGIES CONSIDERED

As part of the examination phase of this study of alternative methods, we have contacted a number of equipment suppliers, developers, and researchers, in both the U.S. and elsewhere.

Key information was obtained on potential methods of PCBs removal from, and destruction in, wastewaters, by cooperative testing between Versar, Inc., and several materials suppliers and process developers. Their assistance is gratefully acknowledged.

We visited the U.S. producer, Monsanto, and several transformer and capacitor manufacturers to ascertain the nature, characteristics and quantities of plant effluents that now contain measureable amounts of PCBs, or might contain PCBs following a spill or other incident. This has provided the background for weighing the advantages and disadvantages of all available technology for potential application to PCBs wastewater treatment. We discussed and evaluated the control methods now used, possible shortcomings, and ideas for more optimized systems.

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In order to find the new technology and approaches that might be forthcoming, we made a computer search of Chemical Abstracts from 1972 to the present, and focused on degradation, decomposition and waste treatment data. Searches were also made of the Lockheed Engineering Index, National Technical Information Service, and Predicasts for information on new developments.

The text reference used as a source of summarized data prior to 1972 was: The Chemistry of PCBs, by Hutzinger, Safe and Zitko, published in 1974 by CRC Press.

Candidate treatment technologies have been divided into the same four categories listed in Section 1.1. Also, as we evaluated technologies, they were placed into categories, as follows, indicating their level of development:

1. Demonstrated Full-Scale Treatments
2. Pilot-Scale Methods
3. Research Approaches to PCBs Removal or Destruction

Some treatment methods were designed for disposal of compounds similar to the PCBs, e.g., chlorinated hydrocarbons and other refractory organics.

The full-scale plant treatments are ready for application to PCB waste problems now. The pilot-scale methods are expected to take one to five years to be developed to the point where they will be determined suitable, or unsuitable, for plant-scale PCBs applications.

Methods currently under development are expected to take three years or more before being ready for plant-scale applications.

Section 2.5 contains a discussion of the applicability of various treatments to the zero discharge objective.

2.1 Treatment of Waste Liquid PCBs and Contaminated Scrap Oils

Only two kinds of treatment or disposal methods are considered suitable for waste liquid PCBs and contaminated scrap oils, and they are now being used. However, there are improvements and design features needed to prevent PCB transfer into the water, air or land.

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2.1.1 Incineration

The standard configuration, long cylindrical steel combustion chamber, having a length to diameter ratio of between 4/1 and 8/1 and well insulated with high alumina refractory brick, is suitable as a primary chamber. Two injectors should be provided: one for a high-BTU gas or fuel oil, and one for the PCB waste liquid. Primary air or steam is provided to vaporize oils, and secondary air is added to complete combustion and provide excess air. These feeds should be made tangentially, or with adequate baffling to assure turbulent flow throughout, and to prevent hot or cold spots in the chamber. It is obvious that almost any residence time may be allowed for a gas flowing through a cylindrical chamber. However, there is a maximum residence time above which turbulence is assured throughout the chamber. Turbulence throughout is assured when wall temperatures are uniform in all parts of the chamber. Most fuel flames provide adiabatic combustion temperatures of about 3000°F. When the more endothermic PCBs are being destroyed, the flame can be rapidly cooled to 2200 to 2500°F; for the very high destruction efficiences desired, 99.999 percent or higher, this is the minimum temperature range required, for a residence time of 3 to 4 seconds. After combustion there should be allowance for afterburning, which may be accommodated in insulated ducts. These can be of sufficient length to assure total residence time of 3 to 4 seconds. Following the combustion phase there must be rapid cooling of the gases, usually by the injection of cold water from a peripheral ring of sprays or jets. Also, the cooling water should be neutralized so that hot hydrochloric acid contact with further components is obviated.

In some systems a high energy venturi scrubber is used to control particulates, if they are expected in the gas stream. In all systems the gas stream is then washed counter currently with water, or water plus neutralizing agent, in some form of a packed tower. Usually a demister is the last element contacted by the gas before it is exhausted through the stack.

The stack gas emissions and the scrubber effluent liquid should be monitored periodically for PCBs levels, and the incinerator should

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have adequate automatic controls to prevent PCBs from being emitted undestroyed. The chief fail-safe control is a pyrometer that causes burner shutdown if the combustion chamber or duct temperature drops below about 2150°F. There are other controls that can warn if such an occurrence might take place. These flow rate controls on the primary and secondary feeds can be monitored so that low fuel flow, or high PCBs-to-fuel flow ratio can indicate a temperature drop. Inadequate air flow can also cause temperature decreases. All such parameters should be monitored, and adequate operator warnings provided. And, of course, to prevent destruction of the venturi scrubber sections, shutdown should automatically take place if cold water flow is ever insufficient.

2.1.2 Sanitary or Scientific Landfill

Sanitary landfilling is an alternative to incineration for PCB users who cannot justify incineration facilities just for PCBs, and who have no waste pickup service organization within reasonable distance. Landfills that will adequately contain PCBs should have all the features described in Section 1.3.3 above, plus there must be assurance that the liquid containers will be sealed and leak proof, and have long life in the landfill.

2.2 Treatment of Wastewaters Containing PCBs

Treatment of wastewaters containing PCBs has received very little attention in practice thus far. Our survey has found a variety of methods for reduction, and even for achieving "zero discharge", of PCBs in wastewaters.

2.2.1 Carbon Adsorption

Carbon adsorption is a well-known water purification and industrial product purification technique. The use of carbon adsorption is well-suited to removing PCBs from wastewater since it is most effective in removing high molecular weight, non-polar, relatively insoluble compounds from water. All these requirements are met by the PBCs.

As will be discussed later, Versar has conducted tests, in cooperation with carbon suppliers, demonstrating the relative effectiveness of

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various activated carbon products. PCB concentrations on the order of 1 ppb were taken as a reasonable effluent objective.

The disadvantage of carbon adsorption is that once used, the carbon may have to undergo destruction by high temperature incineration rather than be regenerated, as is the usual practice. The great advantage of carbon treatment is that a wide spectrum of other toxic organics can simultaneously be effectively removed from water.

Carbon adsorption is currently being used in large-scale municipal water purification systems. Thus capital costs, operating costs and reliability factors are well-known. At the 68th Annual AIChE Meeting in November 1975, G. Strudgeon of Zurn Industries described design features for a 30-million-gallon-per-day carbon system to be built for municipal wastewater treatment at Garland, Texas. This system will cost $5 million, including carbon regeneration. Operating costs are expected to be $6,000 per day.

Although carbon adsorption is the only mechanism thus far proven effective in removing PCBs, three other carbon-based treatment techniques are under study: biodegradation, whereby bacteria-coated carbon particles break down pollutants in wastewater; catalytic action, wherein a very active surface holds pollutant molecules while other degradation or oxidation reactions take place; and chemical reaction, in which carbon is actually depleted as part of a chemical reaction that removes pollutants. The techniques were also discussed at the 68th Annual AIChE Meeting.

As an adjunct to this evaluation study, Versar conducted cooperative laboratory adsorption isotherm tests with Carborundum Company and ICI-US. These tests have extended the ranges of carbon adsorption data published by Calgon Corp. into higher and lower concentrations. Laboratory adsorption isotherm testing is a reliable technique for determining the feasibility of adsorption treatment for PCBs removal from wastewaters and specifically indicates:

1. The effluent levels of PCBs concentration obtainable by adsorption treatment
2. The weight of PCBs adsorbed at the concentrations being studied

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On the other hand, the laboratory test does not determine the necessary contact time for granular carbon beds to effect the desired reduction. This determination is usually performed in small pilot carbon beds under hydraulic flow conditions.

Laboratory and pilot plant tests involving PCBs must be designed to prevent losses of PCBs. The root of the problem is the very low, parts per billion, solubility of PCBs in water. Examples of pathways of experimental loss are:

1. Evaporation to the air
2. Adsorption on a variety of solid surfaces and sediments

2.2.1.1 PCBs Adsorption Testing by Carborundum Company

Versar, Inc., together with Carborundum Co., conducted a preliminary study to determine the ability of an experimental, coal-based activated carbon in removing PCBs from water. This study also provided an analytical check in that both companies made electron-capture gas chromatograph analyses on the same samples, and there was close agreement on results.

The coal-based activated carbon had a surface area of 950 to 1050 square meters per gram. The iodine number was approximately the same as the surface area, indicating that almost all of the pores had a diameter greater than 10 to 15 Angstroms.

The control and test samples were filtered before extraction and gas chromatographic analysis. The removal of PCBs by solids, surfaces, filter media, and the like, was known and expected prior to these tests, thus a high PCB concentration in the filtered control and test samples was the target.

The PCB mixture used was Aroclor 1254. It was solubilized by methanol to give a 1000 ppm stock solution. This was diluted with distilled water to prepare 1000-ppb test solutions.

Table 2.2.1.1-1 presents the data. The filtered control level is considered the actual level the carbon was adsorbing, rather

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TABLE 2.2.1.1-1

CARBORUNDUM CO. TESTS OF PCBs (AROCLOR 1254)
REMOVAL FROM WATER BY AN EXPERIMENTAL ACTIVATED CARBON

Prepared PCBs Concentration (ppb)		Carbon Dosage[1] (mg/l)	PCBs Conc. Before Treatment [Control Conc. After Filtering] (ppb)	Effluent PCB Conc. After Carbon Treatment (ppb)	Percent PCBs Removal
Control -	1000	--	160	--	--
Test	1000	1.0	160	59	63.1
Test	1000	2.0	160	20.6[2]	87.1
				22.0[3]	86.2
Test	1000	10.0	160	2.6[2]	98.4
				2.4[3]	98.5

NOTES: [1] Experimental material, coal-based, 950-1050 square meters/gram.
[2] Versar Inc.'s analysis.
[3] Carborundum Co.'s analysis.

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than the prepared level. The filter removed 84 percent of PCBs in these test runs.

As shown in Table 2.2.1.1-1, the percent PCBs removed from a concentrated water solution (160 ppb) at low carbon dosages was quite good. During plant surveys we found PCBs concentrations in wastewater destined for river discharge to range from 50 to 500 ppb, so the 160-ppb concentration treated in this study was an intermediate value; it was, however, also the highest value treated in the cooperative studies under this program.

Carborundum Co. plans to continue this effort to determine the effects of other carbon dosage levels on various feed PCBs concentrations. The data given here are only considered preliminary.

2.2.1.2 PCBs Adsorption Testing by ICI-US

In a cooperative program with Versar, ICI-US performed preliminary adsorption tests to determine the ability of powdered carbon in removing Aroclor 1254 from water. Versar conducted all analytical tests for this program.

The Aroclor was solubilized with methanol so that a 1000-ppm concentration of Aroclor 1254 in water was achieved. Two types of granular activated carbon were tested: lignite base, and coal base. Both types were ground to a fine powder (90 percent through 325 mesh) before adsorption testing. Prior to grinding, the lignite-base and coal-base carbons had a surface area of about 650 square meters per gram and 1000 square meters per gram, respectively.

The test solutions were made up from distilled, deionized water to a volume of 1 liter. Four levels of Aroclor concentrations were treated: 10 ppb, 100 ppb, 500 ppb and 1000 ppb. Both the control and treated solutions were filtered before analysis. The great affinity of PCBs for all solid surfaces was not fully anticipated, during these tests. The filtration was uniform for all samples through 2.4-cm Reeve Angel fiberglass discs (Grade 934AH). As can be seen in Table 2.2.1.2-1, most of the PCBs were

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TABLE 2.2.1.2-1

ICI-US TESTS OF PCBs (AROCLOR 1254) REMOVAL
FROM WATER BY TWO TYPES OF COMMERCIAL CARBONS

Prepared PCBs Concentration (ppb)	Carbon		PCBs Conc. Before Treatment (Control Conc. After Filtering) (ppb)	Effluent PCBs Conc. (After Carbon Treatment) (ppb)	Percent PCBs Removal
	Type	Dosage (mg/l)			
Control, 10	—	—	1.07	—	—
Test, 10	Lignite[1]	4	1.07	0.177	83.5
Test, 10	Coal[2]	4	1.07	0.190	82.2
Control, 100	—	—	11.15	—	—
Test, 100	Lignite	30	11.15	0.213	98.1
Test, 100	Coal	30	11.15	0.111	99.0
Control, 500	—	—	5.32	—	—
Test, 500	Lignite	100	5.32	0.09	98.3
Test, 500	Coal	100	5.32	0.114	97.9
Control, 1000	—	—	37.5	—	—
Test, 1000	Lignite	100	37.5	0.32	99.2
Test, 1000	Coal	100	37.5	0.24	99.4

NOTES: [1]Larger pore, 650 square meters per gram.

[2]Smaller pore, 1000 square meters per gram.

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removed in filtration. However, by using the filtered "control sample" as an approximation of the amount the filter removes from all feed samples, we can get a good preliminary estimate of the PCBs removal ability of the two kinds of commercial carbons at various wastewater pollutant levels, and at various carbon dosages.

The results of these laboratory tests indicated that powdered carbon was highly effective in removing PCBs from water at four levels from 1 to 40 ppb. There was not a great deal of difference between the effectiveness of the two carbons. The lignite carbon has relatively large pores and smaller surface area than the coal-based carbon. The lignite-based carbon simulates the activity of the coal-based carbon after the latter has a number of thermal regenerations. Thermal regeneration tends to increase the pore size, and lower the surface area of any given carbon. These kinds of activated carbons, however, tend to stabilize at about 550 square meters per gram, even after many regenerations.

The conclusion from these results is that carbon-adsorption can be effective in removing PCBs from wastewaters, even after many thermal regenerations. It is quite significant that in all these tests, the treated effluent PCBs levels ranged from 90 to 320 parts per trillion, which are well below the target maximum PCB level of 1 ppb.

Further testing is needed to get confirmatory isotherm data and column test data. In column tests, the granular form of carbon was used, and, therefore, some of the interior portions of the carbon were not as accessible as they would have been in the powdered form. Thus the tests with powdered carbon, given on a weight fraction basis (i.e., pounds PCBs removed per pound of carbon), yield the maximum weight fraction of PCBs that that can be removed in a scaled-up commercial system.

2.2.1.3 PCBs Adsorption Testing by Calgon Corp.

Adsorption isotherms were run on Aroclor 1242 and 1254. Stock solutions of each compound were prepared in acetone at 100 mg/l.

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Filtrasorb(R) 300 (FS-300) activated carbon was used throughout. Carbon was added from a stock suspension of 1 g or 2 g of pulverized FS-300 per liter of distilled water.

Isotherms of Aroclor 1242 and 1254 were prepared by the following method. Exactly 1 ml of PCB solution was added to seven flasks, each containing slightly less than 1 liter of distilled water. Measured volumes of the 2 g/l carbon stock solution was added to each flask to give carbon concentrations of 0,2,5,10,25,50 and 100 mg/l. The total volume of each flask was 1000 ml. After four hours agitation on a wrist shaker, each solution was filtered through 0.45 micron millipore pads and stored prior to analysis in a refrigerator in quart amber glass bottles having Teflon-lines caps.

A nickel-63 electron capture gas chromatograph was used for analysis; all samples were extracted and concentrated approximately 100 times before analysis. The method is described in the 1971 EPA report, "Methods for Organic Pesticide Analysis in Water and Wastewater."

Table 2.2.1.3-1 shows the PCBs removal data, and gives comparative data for Aldrin. It appears that the Aroclors are removed as effectively as pesticides. Removal from the 50-ppb level to the 1-ppb level seems possible.

Figure 2.2.1.3-1 shows the Calgon data plotted to give the weight percent of PCBs that Filtrasorb-300 carbon can adsorb, at levels down to 1 ppb. As can be seen, the curves take a downward break at about 2 to 3 ppb, indicating that the weight of activated carbon required to remove a unit weight of PCBs is rising rapidly. If this kind of data is confirmed with larger-scale column testing, it would mean that removal of PCBs from water in the parts per trillion range is far more difficult than removal in the parts per billion range.

Also from the figure it can be seen that the initial concentrations (C_o) of the Aroclors were about 100 ppb. However, filtration before testing removed PCBs so that the starting concentrations for the tests were 45 and 49 ppb.

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TABLE 2.2.1.3-1

RESULTS OF CALGON CORP. LABORATORY ISOTHERM TESTS FOR CARBON REMOVAL OF PCBs

Carbon Dosage (mg/l)	Residual (ppb)		
	Aroclor 1242	Aroclor 1254	Aldrin
Control	45	49	48
1.0	--	--	--
2.0	7.3	37	26
2.5	--	--	--
5.0	1.6	17	15
10.0	1.1	4.2	12
12.5	--	--	--
25.0	--	1.6	6.3
50.0	--	1.2	4.4

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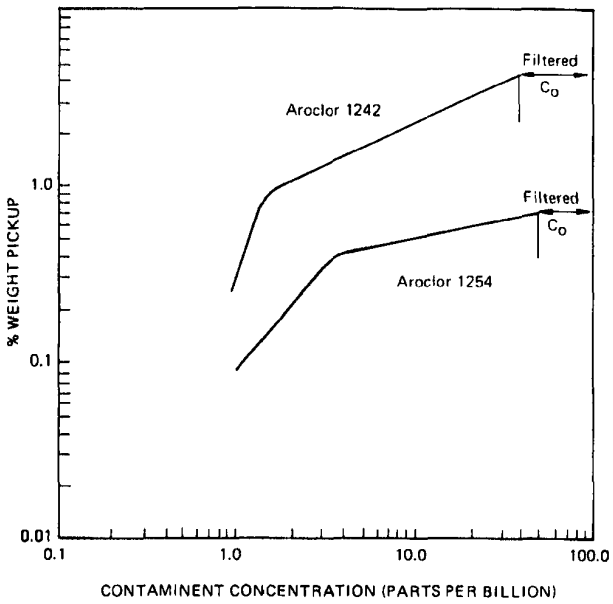

Figure 2.2.1.3-1. EQUILIBRIUM CARBON ADSORPTION OF PCB'S FROM WATER AT LOW CONCENTRATIONS (CALGON DATA)

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Hager and Rizzo of Calgon Corp. have described the essential elements of full-scale adsorption systems in a paper presented to the EPA Technology Transfer Session on Treatment of Toxic Chemicals held in Atlanta on March 19, 1974. Each system is comprised of three basic functional components:

1. The adsorption treatment of the wastewater
2. The carbon reactivation equipment
3. The carbon/water transport arrangement

For PCBs, the practicality of reactivation must be determined.

2.2.1.3.1 Adsorption Treatment of Wastewater

The adsorbers hold the granular activated carbon beds through which the wastewater flows. They can be designed for pressure or gravity flow to achieve the desired contact time of the water with the carbon. Suspended solids and space limitations also must be considered in the adsorber configuration. Flow rates usually fall under 10 gpm per square foot of carbon bed surface area. Contact times for industrial wastewater mixtures usually are in excess of 60 minutes, which is about twice the time employed for purification of domestic sewage. When suspended solids are present, they can be filtered out by the carbon bed; this dual purpose of carbon beds can be usefully employed as long as the adsorbers are designed to accommodate periodic backwashing and bed-cleaning procedures such as air scour and surface wash. For PCBs service, minimum backwashing would be desirable since backwashing would create large quantities of concentrated wastewater needing incineration or treatment. Some settling and prefiltering would be required for optimum system performance.

A well designed water distribution system or underdrain system would insure good backwashing performances, as well as even distribution of water flow. Well established filtration design practices can be effectively employed in carbon bed systems. Carbon beds must be periodically removed via water slurry and obstructions to the flow of carbon from the adsorber should be avoided in adsorber design.

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Carbon beds are normally in excess of 10 feet deep and usually fall into one of four basic configurations:

1. moving beds
2. beds in series
3. beds in parallel
4. expanded beds

The type of configuration selected depends on a number of variables; principal among them are total water flow, suspended solids, and degree of contaminant reduction desired.

2.2.1.3.2 Reactivation of the Granular Carbon

Thermal oxidation, using either multiple hearth furnaces or rotary kilns, is generally employed to reactivate the exhausted carbon. The size of the thermal reactivation equipment is based on the carbon exhaustion rate, i.e., pounds of carbon exhausted per thousand gallons of wastewater treated, and the weight of contaminant on the carbon. Excess capacity is designed into the thermal reactivation unit to allow for variances in carbon use rate due to changes in the wastewater flow and organic loading.

The exhausted granular activated carbon is heated to 1600 to 1800°F to effect volatilization and oxidation of the dissolved organic contaminants. Oxygen in the furnace is normally controlled at less than 1 percent to effect selective oxidation of contaminants over activated carbon. A 5 percent loss of activated carbon per reactivation cycle is an acceptable bench mark upon which to base granular carbon system economics. Particularly for the PCBs, which require an incineration temperature in excess of about 2200°F plus several seconds residence time, the reactivation equipment must include an afterburner. An air scrubber with HCl neutralization would be the last element of the reactivation train. Thus far, the regeneration of carbon used for PCBs adsorption has not been proved.

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2.2.1.3.3 Carbon Transport

Granular spent carbon is usually transported between the adsorbers and the reactivation equipment by water slurry. Various pumping designs can be employed including centrifugal and diaphragm pumps as well as hydraulic or pneumatic pressure. The transport piping should include flush ports and wide radius bends. Typical loading is between 1 and 3 pounds of carbon per gallon of water, depending upon distance and elevation considerations.

2.2.1.3.4 Materials of Construction

Special consideration should be given to the selection of materials of construction with regard to corrosion and erosion.

1. Galvanic Corrosion - Any tendency toward galvanic corrosion due to water characteristics, such as conductivity and pH, will be enhanced in granular carbon beds. Mild steel tanks or adsorbers holding granular carbon under water should be lined. Tanks can also be constructed of cement or reinforced synthetic resins or plastics.

Carbon-in-water slurry piping, which experiences only periodic exposure, is usually exempted from special corrosion considerations.

2. Erosion - Periodic replacement of the carbon beds can cause lining failures at exit ports in carbon tanks and adsorbers. Special grades of stainless steel are usually employed for such wear points.

2.2.1.4 Carbon Regeneration Alternatives - Wet Catalytic Oxidation

For small installations, it might prove feasible to dispose of spent carbon by incineration. Carbon supply companies also offer spent carbon removal services and off-site regeneration.

However, there is a new wastewater treatment technique which might be applicable to carbon regeneration, namely wet catalytic

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oxidation. Several laboratory studies in wet catalytic oxidation are described in Appendix C. Lockheed Missiles and Space Co. (Waste Treatment Systems Section) of Sunnyvale, California, announced in January, 1976, that they have a process ready for pilot plant evaluation and commercial scale-up.

In a preliminary look at the PCBs destruction potential of wet catalytic oxidation, a wastewater sample from an unnamed user of PCBs was subjected to treatment. The PCB mixture approximated Aroclor 1221 most closely, and was very concentrated to 5 ppm in the wastewater sample. Since 5 ppm is much higher than that Aroclor's solubility in pure water, it is believed that solubilizing agents or particulates were carrying most of the PCBs. Within 20 minutes of treatment time, however, about 90 percent of the PCBs had been destroyed, and no large quantities of reaction products were detected. However, this is just one data point and confirmation is needed. The test reactor was a continuously stirred batch system, with air continuously sparged in. The test conditions used were: reactor pressure, 1500 psig; temperature, 550°F; catalyst concentration, 0.5 gram; and reactor volume, 1.5 liters.

The proposed use of wet catalytic oxidation is for carbon regeneration while in spent water slurry form.

Since the capital and operating costs of the catalytic system are tied to the hydraulic load, it might be practical to trap PCBs with carbon in wastewater, and then treat the carbon slurry by catalytic oxidation to destroy the PCBs. In this way, PCBs would be removed from the wastewater by the highly efficient carbon adsorption method, while the volume handled by the catalytic system would be greatly reduced.

Feasibility testing for regeneration of activated carbon by catalytic oxidation is needed. The activated carbon industry has long sought alternatives to thermal regeneration of carbon, because of the loss of carbon by oxidation. With solvent regeneration, or acid or base treatment, the first regeneration only produces about 40 percent of the active surface, which then usually decreases to 30 percent after several more treatments.

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Such degradation is unacceptable. Thus the questions to be answered are: a) Can catalytic oxidation destroy adsorbed PCBs on carbon, converting them to CO_2, H_2O and HCl? b) Will the regenerated carbon have, say, 90 to 95 percent of its original activity? c) Can the process be operated economically? The last question must take into account the necessary operation pressures (500 to 2000 psi), operating temperatures (300 to 650°F), source of oxygen (air, O_2 or ozone), type and lifetime of catalyst, residence time, and materials of construction, among other variables.

2.2.1.5 Further Applications Data

ICI-US provides an excellent booklet entitled "A Symposium on Activated Carbon", providing considerable detail on applications. ICI also provides information on special graphical procedures helpful in the scale-up from isotherm to column testing.

2.2.2 Ultraviolet-Assisted Ozonation

Both UV radiation, and ozone, separately, have been used in water purification for some time. But only in the last five years or so has the synergism of the combination been appreciated in the destruction of organics in water.

Two commercial organizations, Houston Research, Inc., of Houston, Texas, and Westgate Research Corp. of Marina Del Rey, California, are engaged in development of UV-assisted (or catalyzed) ozone oxidation of refractory organics. Both organizations have cooperated in preliminary tests of PCBs destruction, and the method has shown great promise as a large-scale, economic water treatment method. The companies are working mostly with 253.7 nanometer, near-UV, radiation, but they plan to investigate far-UV mercury radiation at 184.5 nm.

It is of particular significance that these methods promise destruction of hydrocarbon organics completely to CO_2 and water. Thus they are likely candidates for zero discharge and total recycle systems.

Related to this is the work of Lawrence at Environment Canada (Burlington, Ontario), who is studying the use of near-UV radiation (about

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365 nm), available from sunlight, in conjunction with titania or alumina photocatalysts rather than the combination of UV and ozone. The ultraviolet region extends to 380 nm, and then blends into visible violet. Studies using visible light are described further below.

UV radiation is generally provided by commercially available tubes, which when operated at low power (and low pressure in the emitting tube) are quite efficient in transferring UV radiation to water. The range of effectiveness is quite short, probably of the order of a few inches maximum, because UV transmissibility in water is poor, and is degraded further by even small amounts of particulate matter.

Ozone is sparged into the reactor, and vigorous stirring is provided until increasing turbulence or mixing power input does not further increase reaction rate.

Various kinds of efficiency values are given to rate different systems, flows, arrangements, etc. For overall efficiency, the units of measure are total organic carbon removed per watt-second of UV input, or per gram of ozone introduced.

Since ozone generation is expensive, work is directed toward optimum use of the ozone introduced. The cost is almost completely that of the electric power used in the silent discharge tube method of making ozone from air. And, of course, UV generation is also an electric power cost factor.

The following subsections discuss UV radiation and its molecular interactions, the photodegradation of PCBs, and UV-assisted ozonation experiments with PCBs.

2.2.2.1 Molecular Responses to Ultraviolet Energy

Energy absorbed in the ultraviolet region (10 to 380 nm) causes electronic transitions within molecules. The principal characteristics of an absorption band are its wavelength and intensity. The wavelength of maximum absorption (λ max) corresponds to the wavelength of radiation having energy equal to that required for an electronic transition. A molar

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absorptivity at maximum absorption (E max) of 10,000 calories per mole or greater is regarded as high intensity absorption. Low intensity absorption is considered an E max of less than 1,000 calories per mole; biphenyl in alcohol at 250 nm has an E max of 18,000, and in hexane at 246 nm, an E max of 20,000.

This would seem to indicate that the basic structure of the PCBs would be readily activated by a mercury lamp generating 253.7-nm radiation. However, this absorption will be modified by the number of chlorine atoms attached to the biphenyl groups. If at any point in the destruction of PCBs, saturated hydrocarbons are formed, they will be unresponsive to 253.7-nm radiation. Saturated hydrocarbons contain sigma electrons exclusively. Since the energy required to bring about ionization of the sigma bonds is of the order of 185 kcal per mole it is only available in the far ultraviolet, below 200 nm. Single carbon-carbon and carbon-chlorine bonds have about the same high bond energy, and are similarly resistant to rupture; however, there is a mercury emission at about 185 nm, which should be capable of activating those bonds, thus making them highly reactive in the presence of oxidizers such as ozone.

Thus it appears possible to produce the excited states in PCB molecules necessary to make them highly receptive to oxidation. Since ozone is a powerful oxidizing agent, and it too is excited in the same regions making it even more effective, the possibilities for a wide range of oxidations are present. This would seem to make complete destruction of PCBs to CO_2, water and HCl feasible.

2.2.2.2 Photodegradation of PCBs

Because of the strength of the C-Cl bond, it has heretofore been assumed that little photochemical cleavage occurs. Further, in the photochemical breakdown of DDT and related compounds, cleavage of the aromatic C-Cl bond is usually not involved. However, Safe and Hutzinger reported in Nature in 1971, that hexachlorobiphenyl photolyzed readily in organic solvents when irradiated at 310 nm. The resultant products are formed by stepwise loss

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of chlorine, rearrangement, and condensation. Other researchers have found that certain pure chlorobiphenyls and PCB mixtures can be decomposed by laboratory UV sources and by sunlight, over long time periods.

The wavelength of the UV radiation appears critical to photochemical decomposition. Low-pressure mercury lamps emitting 254 nm seem to be several times as effective as the UV from sunlight, which is greater than 295 nm. Studies have been carried out in organic solvents and water, and in both liquid and vapor states.

Much of the past work has been on organic solvent solutions of PCBs in order to have high working concentrations. Vapor phase studies have been run to simulate treatment of atmospheric emissions in environmental studies.

Reductive dechlorination, the main photoreaction of chlorobiphenyls, is faster in hydroxylic solvents such as methanol and isopropanol. Even chlorobenzene loses chlorine rapidly on irradiation in isopropanol. Complete dechlorination of a PCB mixture has been observed in 15 minutes in an alkaline isopropanol solution, using a mercury lamp (Anon., Chemical Marketing Reporter, Nov. 6, 1972, page 22). Biphenyl and sodium chloride were identified in the reaction mixture.

Photosensitizers can increase the decomposition rates. Tryptophan, diethylaniline, benzophenone and triphenylene sensitized the photoreaction of dichlorobiphenyl. The reaction was quenched by n-hexyl marcaptan and di-n-butyl sulfide. Experiments in water solution have been hampered by adsorption of the PCBs on the walls of reaction containers, particularly ones made of glass.

Attempts have been made to use surfactants to keep the PCBs in suspension. Adsorption on such solids as calcium carbonate, silica, and soils, in water suspension, has been tested as an aid to photolysis. However, UV radiation will not penetrate deeply into solids, so adsorbed PCB must be kept close to the surface.

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2.2.2.3 Experimental Factors in UV-Assisted Ozone Oxidation of PCBs

For several decades the advantages of ultraviolet radiation in the sterilization of aqueous and dry media have been known. Likewise, the powerful sterilizing, oxidizing effects of ozone have been known. Only with the relatively recent advent of requirements for removing refractory organics from water, and the ability to detect these organics in parts per trillion and even lower concentrations, has the need for powerful oxidizing capability been felt. It was quite natural to combine the two effects into a single treatment or staged treatments, with the result being a strong synergism in many cases.

Enough data has now accumulated to show that UV/ozone wastewater treatment is a powerful method for removal of refractory organics. It has the potential of removing organics to an effective zero discharge level. However, as the decrease in very small concentrations becomes exponential with time, the residence time required in UV/ozone treatment equipment becomes a critical factor. The following variables have been identified as affecting residence time:

1. Molecular structure of the organic
2. Concentration
3. UV transmissivity of the wastewater
4. UV intensity
5. UV wavelength
6. Ozone concentration
7. Liquid turbulence and gas-liquid contact (transfer coefficients)
8. pH
9. Temperature

The following subsections present experimental findings about the relative significance of these variables.

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2.2.2.4 Destruction of PCBs and Refractory Organics at Houston Research, Inc.

2.2.2.4.1 PCB Destruction Data

In preliminary experimentation on the feasibility of PCBs destruction, a high pressure 650-watt mercury tube generating 253.7-nm radiation was used in a 21-liter reactor. Figure 2.2.2.4.1-1 shows the arrangement for a smaller reactor. Oxygen, with an ozone concentration of 2 percent, was sparged in at 3 liters per minute. This was felt to be excess ozone usage, but a good starting point for tests. A 1000-ppm solution of Aroclor 1254 in methanol was used to get a 514-ppb solution of Aroclor 1254 in water. Otherwise the solubility of Aroclor 1254, which is about 50 percent pantachlorobiphenyl, is only 12 ppb in water. It was theorized that significant destruction of this compound would forecast even greater destruction of the other Aroclors now produced, which are all less chlorinated and more soluble in water.

Figure 2.2.2.4.1-2 is a plot of the normalized residual concentration of Aroclor versus time of UV-assisted ozonation. It can be seen that in 1 hour about 2/3 of the PCBs had been decomposed; and in 3 hours, only about 7 percent of the original PCBs remained.

2.2.2.4.2 Operating Data Obtained from Refractory Organics Tests

Houston Research has been studying ozonation for water purification for more than four years. Comparison tests have shown that the addition of UV radiation enhances the reaction rate by 10 to 100 fold. Further it was found that, for the most refractory compound they had tested prior to the PCBs, acetic acid, there was essentially no reaction without UV assistance. However, with UV radiation, the oxidation proceeds rapidly at room temperature.

Figure 2.2.2.4.2-1 shows the effects of UV and temperature on acetic acid destruction. The ordinate is the fraction of total organic carbon remaining, showing that for the 30°C or 50°C tests, with

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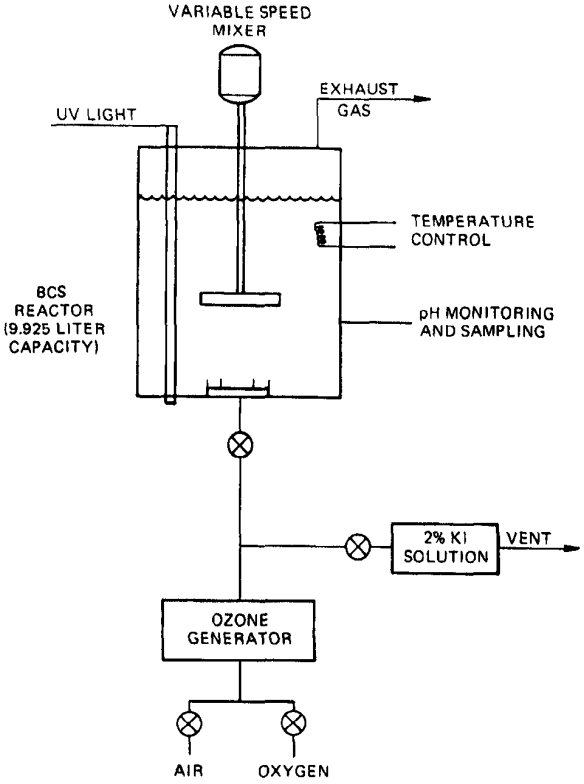

Figure 2.2.2.4.1-1. LAB SCALE APPARATUS FOR REACTION AND MASS TRANSFER STUDIES AT HOUSTON RESEARCH, INC.

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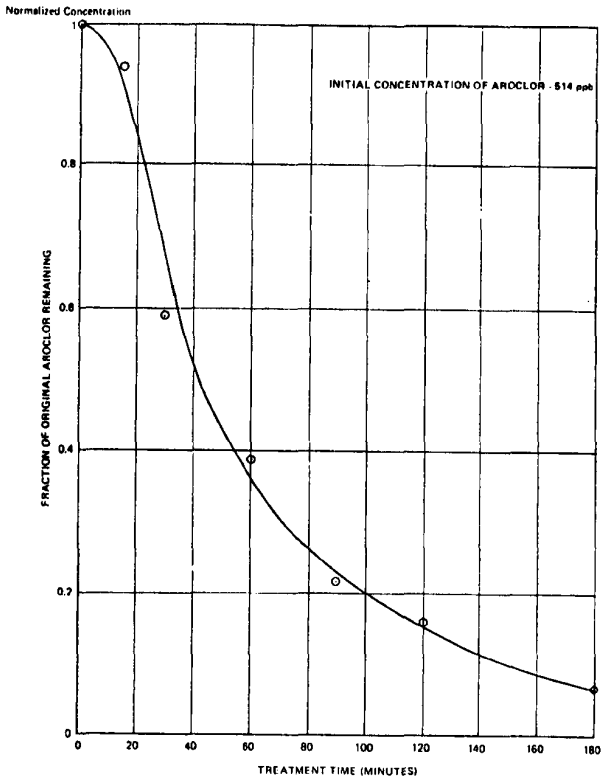

Figure 2.2.2.4.1-2. AROCLOR 1254 DESTRUCTION BY UV ASSISTED OZONATION

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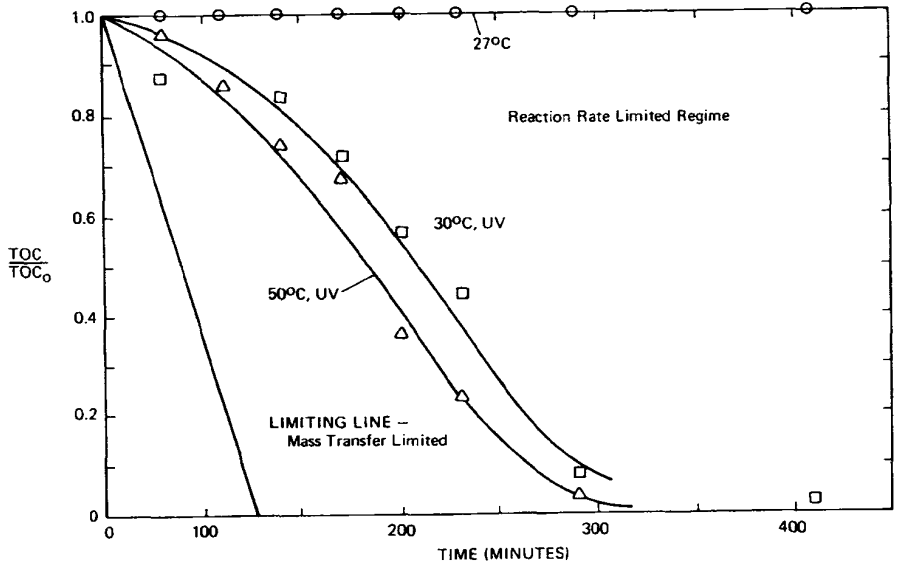

Figure 2.2.2.4.2-1. OZONE OXIDATION OF ACETIC ACID, EFFECT OF UV AND TEMPERATURE (INITIAL CH_3COOH - 105 mg/1, O_3(I) = 3.5 mg/1)

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UV, there is nearly complete destruction to CO_2 and water within 4 to 5 hours The fact that the curves are displaced to the right of the mass transfer limiting line shows that some chemical reaction rate improvement can be sought.

Figure 2.2.2.4.2-2 shows the oxidation improvement achieved by doubling the UV power input, with near constant temperature. Further description may be found in: "Ozone/UV Process Effective Wastewater Treatment", by Prengle, Mauk, Legan and Hewes, in Hydrocarbon Processing, October, 1975.

These are a sampling of the kinds of optimization experiments that must be run with the PCB oxidation system to obtain good economy of design and efficiency of operation.

2.2.2.5 Destruction of PCBs and Refractory Organics at Westgate Research Corp.

2.2.2.5.1 PCBs Destruction Data

Cooperative testing and research between Versar, Inc., and Westgate Research, Inc., determined the effectiveness of Westgate's UV-assisted ozonation process in destroying PCBs. The following experimental conditions were used in the treatment of synthetic wastewaters containing Aroclors 1254 and 1016:

Reactor volume = 3 liters

Reaction time = 4 hours (excess time used to give best chance of destruction)

UV Source = one 43-watt, low-pressure Hg lamp operating at 253.7 nm

Reactor type = vertical, cylindrical, 18 inch long, 3 inch diameter (UV path length = 2 inches)

Pressure = atmospheric

Temperature = 23°C

pH = 6.2

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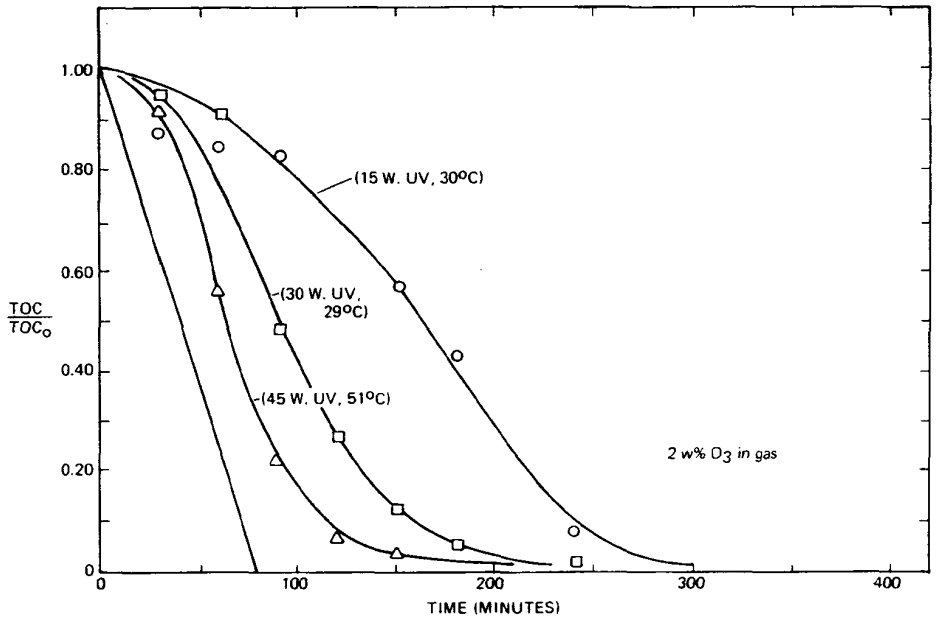

Figure 2.2.2.4.2-2. OZONE/UV OXIDATION OF ACETIC ACID; EFFECT OF INCREASED RADIATION INPUT

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Ozone feed = 70 milligrams ozone/minute in 3.4 liters per minute of oxygen; or about 1.4 percent by weight ozone in oxygen

Reactant preparation = Pure Aroclor 1254 was mixed with an equal portion of methanol, which was then mixed with distilled water to get an apparent true solution. A Hamilton syringe, with vernier calibration giving microliter increments was used to prepare an estimated 200-ppb concentration in a beaker. This solution was added to the reactor (3 liters). Then a 200-ml sample was withdrawn to get the "before" sample.

When preparing the Aroclor 1016 solution, a more concentrated PCBs solution of about 800 ppb was achieved. The before and after treatment concentrations of PCBs are shown in Table 2.2.2.5.1-1.

The data show that the destruction was highly effective in these pioneering tests; more than 99 percent of the original PCBs were destroyed. In addition, the final concentration was at the desired level of about 1 ppb. Such an effluent would be expected to be a reasonable stream for recycle operations and intermediate term zero discharge Potential.

Of course the contact time and ozone expenditure were overly large, but the goal of this preliminary testing was to demonstrate destruction of two key Aroclors in use today.

A more comprehensive study of the UV-ozonolysis of Aroclor 1016 was run, with samples removed from the reactor every 15 or 30 minutes for up to 4 hours. As shown in Table 2.2.2.5.1-2, the initial PCB concentration was 237 ppb. Within 45 minutes the PCB level had been degraded to 1 to 2 ppb, a 99^{+}-percent decomposition. After 2 hours the PCB concentration was less than 100 ppt. The last column in the Table labeled

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Table 2.2.2.5.1-1

UV Ozonolysis Destruction of Typical Capacitor and Transformer PCBs at Westgate Research

	Aroclor 1016	Aroclor 1254
Initial (influent) Concentration (ppb)	790	200
Final (effluent) Concentration (ppb)	0.5	1.5

Table 2.2.2.5.1-2

Destruction of Aroclor 1016 by UV-Ozonation at Westgate Research

UV-Ozonation Time (minutes)	Aroclor 1016 Conc. (ppb)	Chlorinated Products Conc. (ppb)
0	237.0	0.00
15	14.7	33.8
30	7.76	25.86
45	1.73	21.80
60	1.73	18.47
75	0.52	17.63
90	5.2	21.43
120	< 0.1	12.64
150	< 0.1	16.91
180	< 0.1	9.12
210	< 0.1	23.07
240	< 0.1	12.58

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"Chlorinated Products Concentration" is of particular interest. This is the first time quantitative data on the residual compounds in the reaction mixture have been compiled. These residual compounds reach a 33.8-ppb level within 15 minutes from the start of the test and then erratically and slowly drop to about 10 to 20 ppb over the 4 hour period.

The only statements that can be made about these residual compounds is that they are non-PCBs, but chlorinated materials. Possibly a different UV wavelength, or ozone concentration, or the use of a catalyst or other agent could degrade these other products to the non-detectable level.

2.2.2.5.2 Pilot-Scale Tests of Refractory Organics Decomposition

Zeff has described pilot-scale tests of UV-assisted ozonation using 253.7-nm radiation ("UV-OX (TM) Process for the Effective Removal of Organics in Waste Waters", presented at the 68th Annual Meeting of the AIChE, November 20, 1975). This work has grown from a patented invention for a household appliance used to purify tap water. The effectiveness of the method is demonstrated by the reduction in total organic carbon (TOC) of 500 ml of tap water from 5 mg/l to 1 mg/l in 1 minute, using 0.07 mg of ozone and 0.1 watts of 253.7-nm UV. The bacteria plate count was also reduced by a significant amount.

In these studies, batch reaction conditions were optimized to get closest to complete TOC destruction with least O_3 and UV energy input. Then continuous and two-stage operations were investigated. As shown in Figure 2.2.2.5.2-1, a 6-inch-path length of UV was compared with a 3-inch path. In a batch test, the longer path condition took 3 to 4 times as long as the shorter path to achieve the same TOC reduction, in approximate accord with the inverse square law.

The laboratory-scale equipment arrangement is shown in Figure 2.2.2.5.2-2. Table 2.2.2.5.2-1 presents TOC reductions for a 5-part organic mixture under two experimental conditions, showing ozone usage

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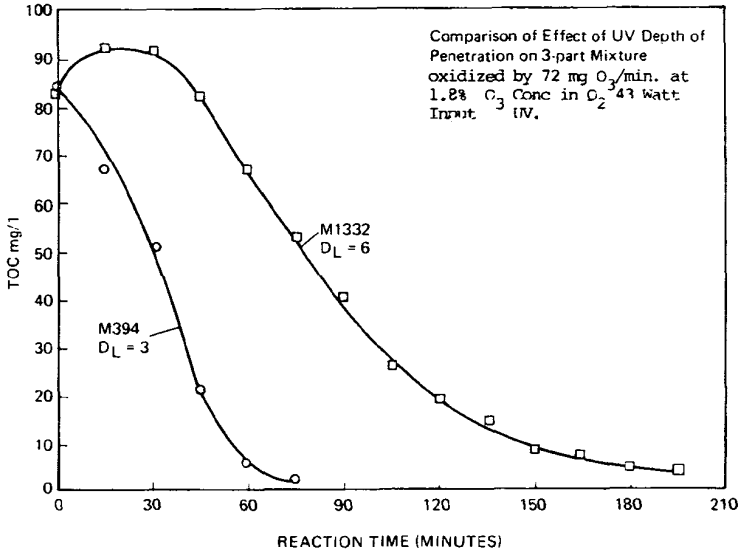

Figure 2.2.2.5.2-1. THE EFFECT OF UV PATH LENGTH ON TOC DESTRUCTION

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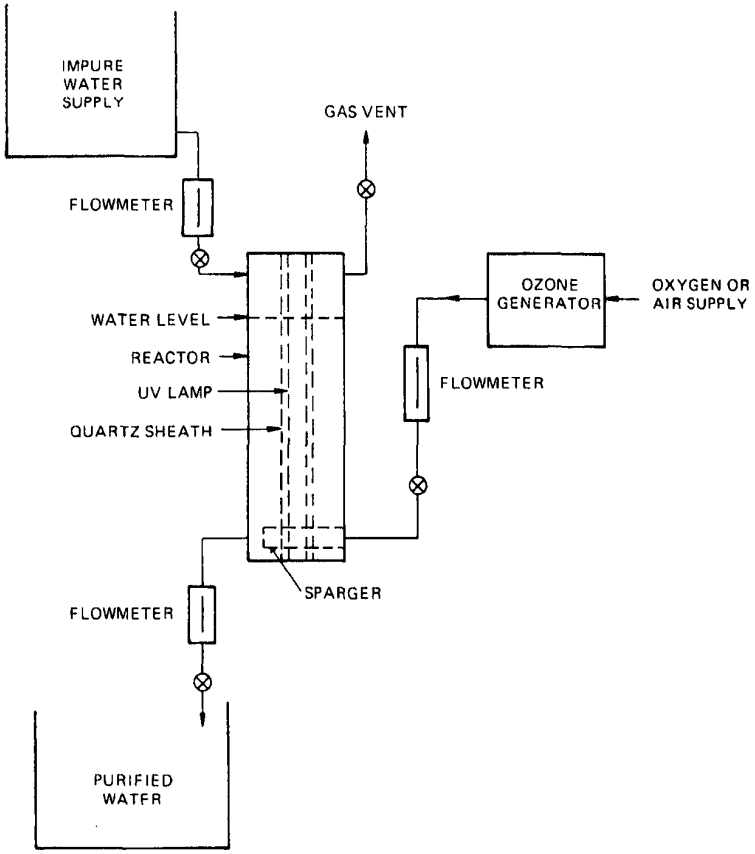

Figure 2.2.2.5.2-2. SCHEMATIC OF BENCH REACTION SYSTEM AT WESTGATE RESEARCH CORP.

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			REACTOR 1							REACTOR 2						OVERALL	
Experiment Number	Influent Conc TOC mg/l	Res Time/Recl min	Input O_3 Conc % by wt	Input O_3 Mass Flow mg/min	Output O_3 Conc % by wt	Output O_3 Mass Flow mg/min	Effluent TOC Conc mg/l	Ave Rate of TOC Removal mg/min	UV Index w-m/mgC	Supplied TOC/O_3 Effic %	Input O_3 Conc % by wt	Input O_3 Mass Flow mg/min	Output O_3 Conc % by wt	Output O_3 Mass Flow mg/min	Effluent TOC Conc mg/l	Ave Rate of TOC Removal mg/min	UV Index w-m/mgC	Supplied TOC/O_3 Effic %	Ave Rate of TOC Removal mg/min	UV Index w-m/mgC	Supplied TOC/O_3 Effic %
S341	39.0	80	2.5	124	1.3	65	9.0	4.5	9.6	29.0	2.5	124	1.5	74	5.0	0.6	46.7	3.9	2.5	13.9	16.4
S342	75.5	48	2.7	171	1.8	113	21.0	13.6	3.2	63.7	2.7	171	1.9	120	6.0	3.7	7.5	17.5	8.7	4.1	40.6

TABLE 2.2.2.5.2-1

Simulated Two-Stage, Continuous UV-Ozonation of a 5 Component Mix at Westgate Research Corp.

(43 watt UV Input Reactor 1)
(28 watt UV Input Reactor 2)

efficiencies, and energy usage efficiencies, with a simulated two-stage continuous operation. Zeff has calculated the prime energy costs for UV-assisted ozonation based on a scale-up of a pilot reactor. The pilot reactor handled 20 gph, so that 210 of these units in parallel would handle 100,000 gpd. The plant area needed for this equipment would be only 18 feet square, with a height of 3 feet.

Based on pilot tests of this reactor, it might be assumed that it could convert wastewater of 40 mg/l TOC to less than 5 mg/l, using six 43-watt UV lamps. It is assumed that a UV energy requirement of 5 watt-minutes per milligram of carbon oxidized will suffice. Also, the ozone requirement will be 2 moles per gram-atom of carbon oxidized, but at a 75-percent efficiency, or 2/.75 = 2.67 moles ozone per gram-atom of carbon. Assuming a power cost of 1.5¢/KWH; the ozone generating power cost would be $53.40 and the UV power would be $18.93; or a total of $72.33 per 100,000 gal. of water treated.

Zeff points out that the 210 reactor modules would require 1260 43-watt lamps (six per reactor). This appears to be a large number of lamps, but it is actually very practical. Such arrays of lamps are regularly used for room illumination in factories and large offices, and the low-pressure mercury lamps used here are nothing but fluorescent lamps without the phosphor coating. An extended array such as this is much more energy-efficient than fewer high-power high-pressure industrial UV irradiators; and maintenance and replacement of lamps is much simpler. The life of the low-power lamps is 7500 hours as compared to 1000 hours for the high-power lamps.

2.2.2.6 Laboratory Test Results from AiResearch Corporation

In the laboratory tests of the AiResearch Corporation, high-pressure 450-watt mercury lamps were used. The test solutions were very dilute mixtures of methanol, ethanol, isopropanol, and acetone in water. The ozone was introduced into the 4-liter organic mixture in an oxygen stream bubbled in at 2 liters per minute; ozone concentration in the oxygen was 33 mg/liter. With the expenditure of 7.9 grams of ozone, the mixture of alcohols and acetone was reduced from 115 mg/l COD to 10 mg/l in 2 hours.

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2.2.2.7 Comments on UV/Ozone Tests

These highly encouraging tests by three different companies in the destruction of some of the most refractory organics encountered in wastewater treatment, give confidence that scaled-up systems can adequately destroy PCBs in industrial wastewaters. The next step required is detailed cost effectiveness testing in pilot-scale equipment.

2.2.3 Non-Carbon Adsorbents for PCBs

A variety of non-carbon materials, some well-known for treating water and some that seem to be quite specific for PCBs removal, have been found. Limited cooperative laboratory testing of PCBs removal has been conducted in order to gain insight into potential effectiveness.

Materials considered or examined were:

1) Rohm and Haas Amberlite XAD series resins - These were laboratory-tested for PCBs removal
2) Polyvinyl chloride - Tested by Canadian investigators for PCBs removal
3) Clays and Humus - Tested by Monsanto for PCB removal
4) Polyurethane - Tested by Canadian, Swedish and other investigators for PCBs removal
5) Sphagnum Peat - Used in commercial water purification, but has not been tried with PCBs
6) Polyelectrolytes as flocculating agent - Not really adsorbents, but could be aids to removing finely divided adsorbents from treated wastewaters; have not been tested
7) Coal - Not tested with PCBs, but being experimentally used for water treatment
8) Molecular Sieves - Not tried with PCBs, since they were judged to be of improper character; they would be expected to preferentially remove water from PCBs, rather than PCBs from water
9) Miscellaneous Sorbents - A number of proprietary Oil Sorbents, such as the "3M Brand" series, that were not tested with PCBs, might have some application

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2.2.3.1 The Amberlite XAD Series of Macroreticular Resins

2.2.3.1.1 PCBs Adsorption Testing

Cooperative preliminary experimental work was carried out between Versar and Rohm and Haas to test the PCB-adsorption capacity of XAD-4 resins. The tests confirmed the effectiveness of this resin (see Appendix D).

Since carbon adsorption is the more established technology for removal of organics, it was felt that a side-by-side comparison of a carbon and an Amberlite resin would be useful.

These tests showed that resin and carbon are comparable in PCBs removal effectiveness. The resin method includes on-site regeneration, with the concentrated waste PCBs treated by incineration. Details on the apparatus and materials used by Rohm and Haas and the results of their experiments are given in Appendix A.

2.2.3.1.2 Process Concept for Resin Adsorption of PCBs

Based upon the experiments described in Appendix A, the Rohm and Haas experience has led them to envision the following plant-scale process, subject to further experimentation.

The wastewater to be treated is passed through one or more columns, each containing polymeric adsorbent. Once the resin is loaded to capacity with PCB, it is taken off line for regeneration. A water miscible solvent is usually used for regeneration, and is in turn displaced from the adsorbent by water. The stream resulting from this operation is carefully fractionated to optimize solvent recovery. The final rinse usually contains a very low level of solvent in water and this must be collected as a PCBs wastewater.

The distillation column permits solvent recovery at high purity, leaving water and PCB in the bottoms. To minimize

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distillation costs, a patented variation of the process, called "superloading", is used to maintain a high PCB concentration in the final toxic material to be disposed. Part of this process includes a separator from which the organic phase is PCB while the aqueous phase is recycled to "superload" the adsorbent. A completely enclosed system can readily be designed to insure minimum operator exposure to PCB. A process concept flow sheet of such a PCBs removal system is shown in Figure 2.2.3.1.2-1.

The experimental work necessary to plant-scale design is as follows:

1. More extensive leakage data should be gathered for XAD-4 and other Amberlite polymeric adsorbents, encompassing several influent concentrations of PCBs; other Aroclors should also be tested.
2. The ability of the Amberlite polymeric adsorbents to be solvent regenerated should be demonstrated and the optimum solvent determined
3. The capacity of the Amberlite polymeric adsorbents should be determined over a number of loading/regeneration cycles to see the effect, if any, of long-term operation on capacity.

The description of XAD-4 resin and its comparison with other Rohm and Haas resins that might also have application to PCBs removal are given in Appendix B.

Further descriptions of non-carbon adsorbents are presented in the Appendix C. They contain relevant experimental work on PCBs and refractory organics, and are included to give a more complete picture of the options assessed under this program. Also included in Appendix C are summaries of catalytic reduction, catalytic oxidation, microorganism studies, ultrafiltration, and reverse osmosis. For the removal of PCBs from wastewater, all are considered to be in the research stages. Several have potential for contributing to zero discharge technology.

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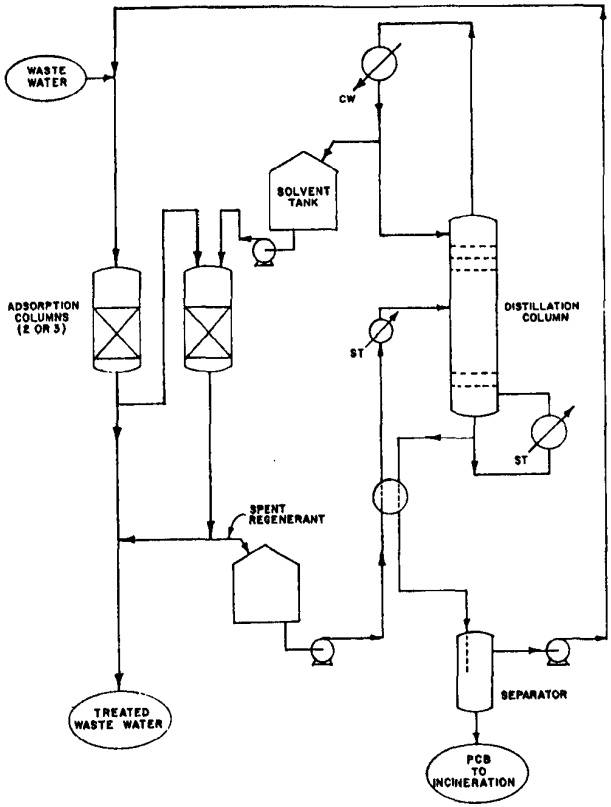

Figure 2.2.3.1.2-1
PCBs REMOVAL PROCESS CONCEPT FLOW SHEET
BY ROHM AND HAAS COMPANY

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2.3 Treatment of PCBs - Contaminated Solid Wastes

2.3.1 Incineration

Incineration has been described in Section 1.3.3. For the variety of solids ranging from granular particulate, such as fuller's earth, to large chunks of solids, such as transformer internals, the best destruction method is rotary kiln incinerator, followed with adequate afterburning to prevent PCB vaporization.

2.3.2 Sanitary Landfill

The best technology for segregation of the PCBs solid wastes so that spillage, leakage to waterways, or emissions to the atmosphere will not occur, is described under Section 1.3.3.

2.4 Treatment of Air Emissions

2.4.1 Condensation Methods

Our survey found one plant that was practicing chilling of exhaust gases from PCBs processing areas. With the low vapor pressure of PCBs even at room temperature, it might be expected that they could be effectively swept out of chilled air with the condensing water. Undoubtedly this does occur to some extent; however, the high activity coefficients of PCBs tend to keep them vaporized at levels near their pure liquid vapor pressure at that low temperature. Previous work by Versar has shown that PCBs in stack emissions from sludge incineration are not removed by water scrubbing (EPA Contract 68-01-1587).

2.4.2 Granular Adsorption Methods

Although no information was uncovered on the collection of PCBs from air streams by any form of granular filter, it would be expected that such treatment should be effective. In fact, it would be expected that the same adsorbents discussed under Sections 2.2.1 and 2.2.3 above would be the most effective. Activated carbon removal of organic vapors has been practiced in such widely divergent circumstances and devices as gas masks, kitchen range hood systems, and submarine air recycle systems.

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2.4.3 Catalytic Oxidation of Organics in Evaporated Effluents

Studies of vapor phase oxidation show the potential for PCBs destruction in air exhausts at lower than incineration temperatures. Catalysts would have to be resistant to HCl vapors, but fuel savings and insulation savings would be large. This procedure should be amenable to all proportions of water and organics in such air streams.

Borkowski passed PCB vapors over a catalyst at elevated temperatures ("The Catalytic Oxidation of Phenols and other Impurities in Evaporated Effluents," Water Research (1); 367 (1967)). Copper oxide was the most active of a large number of catalysts tested and oxidation to carbon dioxide and water appeared to be complete at temperatures over 300°C and at residence times of about 0.08 seconds. Without the catalyst, 1000 to 1200°C was required to achieve the same degree of removal.

Walsh and Katzer studied contaminated air-water vapor streams over supported copper oxide and showed that the rate was first order in phenol and relatively rapid between 150 and 270°C ("Catalytic Oxidation of Phenol in Dilute Concentration in Air", Ind. Eng. Chem. Process Design Develop, (12); 477 (1973)). At 150°C and a space velocity of 4100 hr^{-1} the phenol conversion was 99.6 percent, and there was little evidence of any intermediate organics in the condensate.

These methods of air purification are in the research stages, and actual testing of PCBs in air is required.

2.5 The Potential for Zero Discharge

The best method of achieving zero discharge, in the face of the practical problem of defining what a zero concentration is, is to establish total recycle. This appears feasible for wastewater, but not for solids or air emissions. Fortunately, for solids, incineration technology promises very high efficiency of destruction simply by setting the temperature and residence times high enough.

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For air emissions, although vapor pressures are low for PCBs, large surfaces have the potential for giving off significant quantities of PCBs. Versar research has found powerful adsorption and destruction methods for organics in air. If destruction equivalent to that achieved by incineration can be achieved at lower temperatures through catalyzed reactions, near zero emissions are possible.

For wastewater recycle, methods of adsorption and catalytic destruction promise PCBs reduction to levels low enough such that reuse is practical. Our survey has shown some municipal and fresh waters contain PCB concentrations of 1 ppb or greater, and many river waters can contain many times that. Thus the recycled water at 1 ppb of PCB would be very suitable for reuse.

3.0 RATIONALE AND SELECTIONS OF CURRENTLY RECOMMENDED WASTE TREATMENT METHODS

Based upon our plant surveys of the PCB-using capacitor and transformer manufacturers, the single U.S. PCB manufacturer, and waste treatment equipment suppliers, and upon the analysis and evaluation of all available technologies whether in commercial use, pilot plant, or research stages, Versar has developed recommendations for the most practical treatment methods available now. We have also made predictions of methods applicable over the short- and long-term future. Our current recommendations are based on technology that is either currently in use and doing an excellent job of PCB destruction or removal, or holds great promise of doing that job based upon success in similar but non-PCB, applications.

3.1 Incineration Recommended for Liquid PCBs and Scrap Oils

For liquid PCBs and contaminated scrap oils, we determined only two candidate methods: incineration and sanitary landfill. It is possible that some chemical degradation methods discussed under wastewater treatment might later become applicable to concentrated PCB liquids, but the prospect is not clear at this time.

Sanitary landfill is not recommended for liquids when incineration is available. The potential for liquids escaping in large quantities from ruptured

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containers, caused by any of a number of circumstances, and then causing massive leaching and liquid control problems at the landfill, is felt to be too great.

Incineration, on the other hand, offers a straight-forward and physically simple method of final destruction. Incineration facilities that have successfully handled PCB liquids are available in Massachusetts, New York, Delaware, Illinois, Texas and Louisiana. Pilot or experimental facilities are available in other parts of the country. With the increase in requirements for disposing of many other liquid organics, it is expected that new facilities suitable for PCBs destruction will be added.

Versar therefore recommends incineration, particularly if there is a choice of the kind of disposal facility to be constructed.

3.2 Carbon Adsorption and UV-Assisted Ozonation Recommended for PCBs in Wastewater

Our survey of wastewater treatment technology was extensive and excellent potential for current, near- and long-term methods was found. The longer term pilot- or research-scale methods hold great promise for achieving zero discharge.

For wastewater treatment, Versar's recommendation is carbon adsorption. This technology has been well proved in a wide variety of industrial adsorption problems. It is constantly being successfully applied to the removal of new organics from water. Our cooperative laboratory work with several suppliers has confirmed preliminary reports of success in removing PCBs. All of the aspects of commercial carbon adsorption, from favorable capital and operating economics to reasonable operating methods, materials of construction, and lack of transport of pollution to air or land, have been proven for PCB-like materials. There is every reason to expect commercial success with PCB removal from wastewater.

Potential problems with carbon adsorption includes the collection of backwash water and spent carbon for incineration or other treatment. With these limitations in mind, we studied the various alternatives and have determined

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that the UV/ozone method is the best. However, it must be appreciated that this technology is still somewhere in the pilot-plant and research stage, but our cooperative testing with two equipment suppliers shows the method to be effective in destroying PCBs. It offers the potential of degrading breakdown products all the way to CO_2, water and HCl. Any kind of process that generates no solids or liquids for later disposal must be considered for application where no wastewater treatment facilities now exist, and where facilities for incineration of carbon system wastes are not convenient.

The major factors yet to be determined for the UV/ozone systems are costs and operating practicality. Separately, UV and ozone systems are being used in commercial applications, and it is therefore anticipated that the combination will be practical. Choices of the proper UV-radiation wavelength and power levels still need to be made, as well as methods of improving ozone-use efficiency. It appears that commercial UV and ozone generators are suitable.

3.3 Incineration and Landfill Recommended for Contaminated Solids

Although incineration is recommended for PCB contaminated solids, because of its final destruction capability and prevention of any long-term problems, sanitary or scientifically-controlled landfilling must be considered a close second choice. At present, the only incineration facilities for handling the full spectrum of PCB-contaminated solids are those of Rollins Environmental Services in Delaware, Texas and Louisiana. This limitation on locations for treatment requires that the alternate, landfill, be considered.

Landfill, as practiced by Chemtrol Corp., appears perfectly suitable for containment of PCB-contaminated solids, at least over a medium term. Our reservation with this method is that it might be relegating a problem to the future. Our concern is that some decades in the future, when a landfill might be closed, no agency will be prepared to handle the sump emptying and maintenance necessary to prevent leaching. We anticipate that some time in the future, many landfills will have to be mined, and final destruction or recovery carried out for land use or hazard reasons.

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3.4 Dry Carbon Filter Adsorption Recommended for Control of Air Emissions

For much the same reasons listed in Section 3.2, we recommend that current emissions of PCBs in plant air be trapped in carbon-containing filters. It is recognized that other and better adsorbents may emerge from research, as described in Section 2.2.3, but it is felt that such advances will be readily applicable to any kind of filter pack, screen or cartridge system already in use.

The long record of proven capability of carbon adsorption is the main factor in its choice. However, since contaminated carbon must be either incinerated or regenerated, over the longer term we see the use of low-temperature catalytic oxidation methods as described in Section 2.4.3. Catalytic oxidation methods hold promise for near zero discharge, with the generation of no solid wastes.

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SECTION VII

PRODUCTION AND DISTRIBUTION

1.0 PRODUCTION AND CURRENT USE

1.1 Domestic Production of PCBs and PCTs

Currently there is only one known commercial scale PCB production installation in the U.S., the William G. Krummrich plant of the Monsanto Chemical Company in Sauget, Illinois. This facility is specifically designed for chlorobiphenyls production and has a design capacity of 48 million pounds per year.

Until 1971 PCBs were also manufactured at Monsanto's Anniston, Alabama plant which had a design capacity approximately equal to the Sauget plant. The Alabama operation was discontinued and the plant dismantled in 1971.

PCBs manufactured by Monsanto are marketed under trade name "Aroclor". Tables 1.1-1 and 1.1-2 present data from Monsanto related to production and sales of PCBs from 1957-1974 and production of polychlorinated terphenyls (PCTs) from 1959-1972. The production of PCTs were terminated in 1972. Until then in addition to PCBs (Aroclor series 12) Monsanto manufactured Aroclors 2565, 4465, 5442 and 5460. Aroclors 2565 and 4465 were blends of PCBs and PCTs and Aroclors 5442 and 5460 were two different grades of PCTs. Also given in these Tables are breakdowns of domestic sales per use category and by PCB grade. Detailed information and breakdown on PCB/PCT blends and PCT grades is not available. However, Monsanto reports that the predominant material produced was Aroclor 5460. When produced and marketed these materials were used in plasticizer applications. Figures 1.1-1 through 1.1-3 are graphical representations of these data.

As can be seen from Figure 1.1-1, the majority of the PCBs produced in the United States was marketed domestically. Production and sales of PCBs in 1974 were less than half of those for 1970, where production and sales of PCBs were at their maximum. The difference between production and sales on

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TABLE 1.1-1

PCB & PCT MANUFACTURE AND PCB SALES

MONSANTO INDUSTRIAL CHEMICALS COMPANY

1957 thru 1964
(Thousands of Pounds)

	1957	1958	1959	1960	1961	1962	1963	1964
U.S. PRODUCTION OF PCBs	(1)	(1)	(1)	37919	36515	38353	44734	50833
DOMESTIC SALES OF PCBs	32299	26061	31310	35214	37538	38043	38132	44869
U.S. EXPORT SALES OF PCBs	(2)	(2)	(2)	(2)	(2)	(2)	3647	4096
U.S. PRODUCTION OF PCTs	-	-	2996	3850	2322	4468	4920	5288
DOMESTIC SALES OF PCBs BY CATEGORY								
Heat Transfer	-	-	-	-	-	157	582	929
Hydraulics/Lubricants	1612	1549	2685	2523	4110	3915	3945	4374
Misc. Industrial	704	755	1569	1559	2114	1681	1528	1692
Transformer	12955	5719	5984	7921	6281	7984	7290	7997
Capacitor	17028	14099	16499	16967	15935	15382	15606	19540
Plasticizer Applications	(1)	3939	4573	6244	9098	8924	9181	10337
Petroleum Additives	-	-	-	-	-	-	-	-
DOMESTIC SALES BY PCB GRADE								
Aroclor 1221	23	16	254	103	94	140	361	596
Aroclor 1232	196	113	240	155	241	224	13	13
Aroclor 1242	18222	10444	13598	18196	19827	20654	18510	23571
Aroclor 1248	1779	2559	3384	2827	4023	3463	5013	5238
Aroclor 1254	4461	6691	6754	6088	6294	6325	5911	6280
Aroclor 1260	7587	5982	6619	7330	6540	6595	7626	8535
Aroclor 1262	31	184	359	326	361	432	414	446
Aroclor 1268	-	72	102	189	158	210	284	190
Aroclor 1016	-	-	-	-	-	-	-	-

(1) Production figures and Plasticizer Applications figures unavailable during year indicated.
(2) U.S. Export Sales figures unavailable during year indicated.

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TABLE 1.1-2

PCB & PCT MANUFACTURE AND PCB SALES

MONSANTO INDUSTRIAL CHEMICALS COMPANY

1965 thru 1974
(Thousands of Pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
U.S. PRODUCTION OF PCBs	60480	65849	75309	82854	76389	85054	34994	38600	42178	40466
DOMESTIC SALES OF PCBs	51796	59078	62466	65116	67194	73061	34301	26408	37742	34406
U.S. EXPORT SALES OF PCBs	4234	6852	8124	11231	10624	13651	-	6388	8346	5395
U.S. PRODUCTION OF PCTs	6470	8190	9450	8870	11600	17768	20212	8134	-	-
DOMESTIC SALES OF PCBs BY CATEGORY										
Heat Transfer	1237	1766	2262	2529	3050	3958	3060	752		
Hydraulics/Lubricants	4616	4258	4643	5765	8039	7403	1552	0		
Misc. Industrial	1841	1779	1426	1283	1079	1627	1155	0		
Transformer	8657	8910	11071	11585	12105	13828	11134	25656	37742	34406
Capacitor	23749	28884	29703	29550	25022	26708	14141			
Plasticizer Applications	11696	13481	13361	14404	16460	19537	3259	0		
Petroleum Additives	-	-	-	-	1439	-	-	0		
DOMESTIC SALES BY PCB GRADE										
Aroclor 1221	369	528	442	136	507	1476	2215	171	35	57
Aroclor 1232	7	16	25	90	273	260	171	0	0	0
Aroclor 1242	31533	39557	43055	44853	45491	48588	21981	728	6200	6207
Aroclor 1248	5565	5015	4704	4894	5650	4073	213	807	0	0
Aroclor 1254	7737	7035	6696	8891	9822	12421	4661	3495	7976	6185
Aroclor 1260	5831	5875	6417	5252	4439	4890	1725	305	0	0
Aroclor 1262	558	768	840	720	712	1023	1	0	0	0
Aroclor 1268	196	284	287	280	300	330	0	0	0	0
Aroclor 1016	0	0	0	0	0	0	3334	20902	23531	21955

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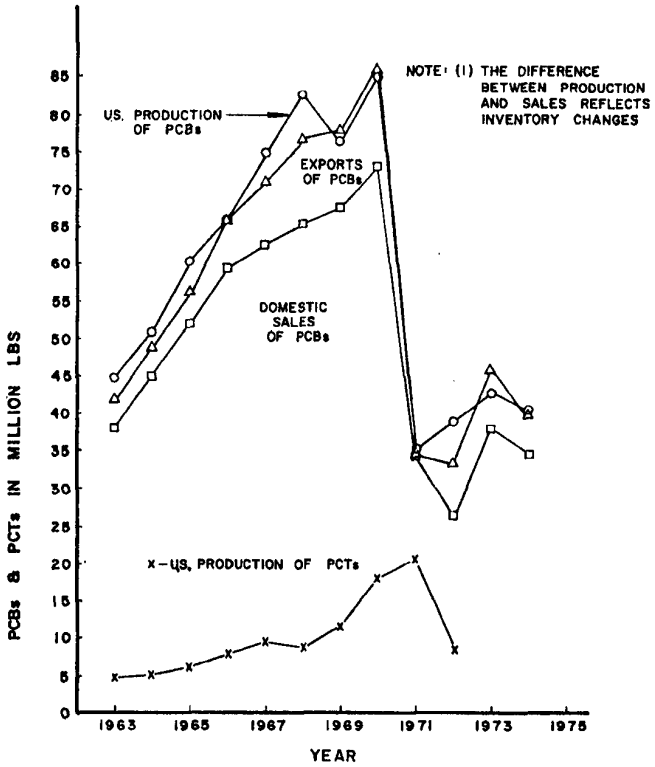

Figure 1.1-1 - U.S. Production of PCBs and PCTs and Domestic Sales and Exports of PCBs

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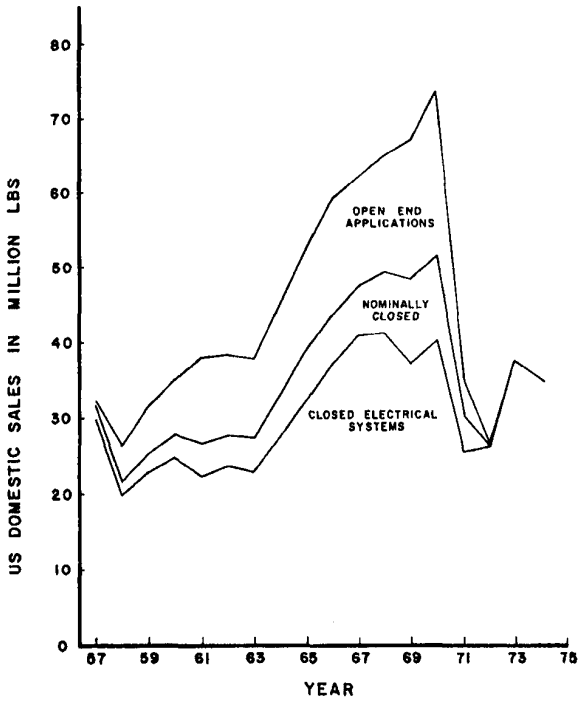

Figure 1.1-2 - U.S. Domestic Sales of PCBs by End Use Applications

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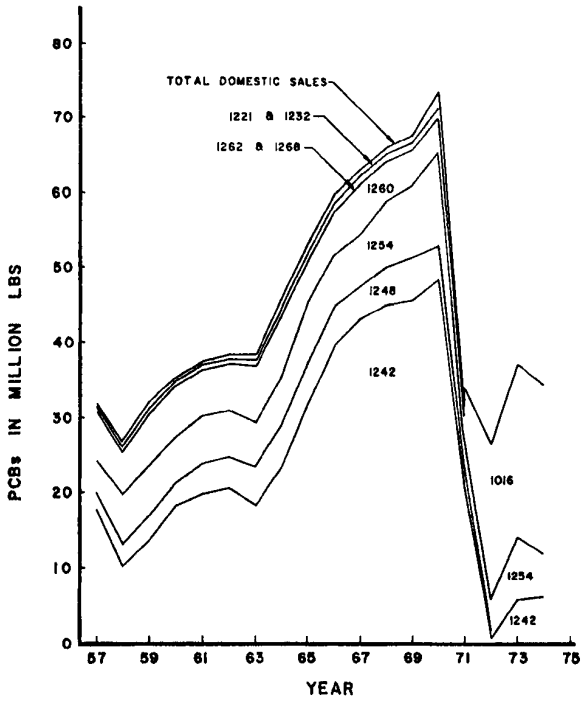

Figure 1.1-3 - U.S. Domestic Sales of PCBs by Type

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this graph reflects inventory changes of PCBs. Figure 1.1-1 also indicates that the production of PCTs increased steadily through 1971 when their production was at the maximum. The production of PCTs was terminated in 1972.

Table 1.1-3 shows production, sales and export of PCBs for the first quarter of 1975. Monsanto reports that sales for Aroclor are expected to increase at an average annual rate of 6-7 percent over the next few years. Additionally, exports of Aroclor are expected to maintain the same ratio to the U.S. production as in the past.

Figure 1.1-2 indicates that prior to Monsanto's voluntary restriction of sales to all applications with the exception of "closed electric systems", approximately 13 percent of the PCBs in the U.S. was used in "nominally closed" applications (heat transfer, hydraulic fluids and lubricants) and 26 percent was used in "Open End" applications (plasticizers, surface coating, ink, adhesives, pesticide extenders, and microencapsulation of dyes for carbonless duplicating paper) where entries of PCBs to the environment are more probable and PCB emissions are uncontrollable. At present, almost all domestic production is being used in "closed electric systems" (transformer and capacitor applications) where PCB emissions are more controllable.

Between 1957 and 1971 there were twelve different types of Aroclor manufactured by Monsanto with chlorine contents ranging from 21 to 68 percent. Aroclor 1242 and grades lower than 42 percent chlorine made about 48 percent of the total production consumed. U.S. Sale of Aroclor 1242 has dropped drastically since 1971 and has been replaced by Aroclor 1016. Sales of Aroclor 1254 remained about the same for the period 1957 - 1974. Currently, there are four different types of Aroclor manufactured by the Monsanto Company-Aroclors 1221 and 1016 for capacitor applications and Aroclors 1242 and 1254 for transformer applications.

Past and current end-use of PCBs by types are presented in Table 1.1-4. In the years prior to 1971 the largest "open-end" use of PCBs and PCTs has been in plasticizer applications. According to Monsanto, a large percentage of the production of Aroclor 1242 and lower chlorine content grades and the entire PCT production were used for this application. Following Monsanto's

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TABLE 1.1-3

PCB MANUFACTURE AND SALES
MONSANTO INDUSTRIAL CHEMICALS COMPANY
First Quarter - 1975

	(Thousands of Pounds)
U.S. PRODUCTION	8532
DOMESTIC SALES	7986
U.S. EXPORT SALES	1538
DOMESTIC SALES	
Transformer and Capacitor	7986
DOMESTIC SALES BY PCB GRADE	
Aroclor 1221	10
Aroclor 1242	2201
Aroclor 1254	2115
Aroclor 1016	3660
PREDOMINANT UTILIZATION OF AROCLORS	
Aroclor 1221	Capacitors
Aroclor 1016	
Aroclor 1242	Transformers
Aroclor 1254	

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TABLE 1.1-4

END-USES OF PCTs AND PCBs BY TYPE

End-Use	1016	1221	1232	1242	1248	1254	1260	1262	1268	PCTs
Existing Sales										
Capacitors	XX	X		XX through 1971		X				
Transformers				X		XX	X through 1971			
Sales Phased-Out										
Heat transfer				X						
Hydraulics/ lubricants										
. hydraulic fluids			X	X	X	X	X			
. vacuum pumps					X	X				
. gas-transmission turbines		X		X						
Plasticizers										
. rubbers		X	X	XX	X	X			X	
. synthetic resins					X	X	X	X	X	XX
. carbonless paper				XX						
Miscellaneous Industrial										
. adhesives		X	X	XX	X	X				XX
. wax extenders				XX		X			X	XX
. dedusting agents						X	X			
. inks						X				XX
. cutting oils						X				
. pesticide extenders						X				
. sealants & caulking compounds										XX

Notes: (1) X denotes use of a given Aroclor in a specific end-use, while XX denotes principal use
(2) PCTs denote series 25,44 & 54 Aroclors

Source: Monsanto Industrial Chemical Co.

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voluntary restrictions in 1972, Aroclor sales for plasticizer applications dropped to small percentage to that of the previous years. Historically, capacitors have always been the single largest PCB use category except for the years 1969-1971 when Aroclor usage for plasticizer applications was higher. The major uses of PCBs prior to 1969 in order of volume of material used is listed below:

- Capacitors
- Plasticizers
- Transformers
- Hydraulic fluids and lubricants
- Heat transfer fluids

1.2 Foreign Production and Distribution of PCBs

Known current foreign producers of PCBs are the United Kingdom, Czechoslovakia, France, Germany, Italy, Spain and the U.S.S.R. Detailed information on total production of PCBs outside the U.S. is not available. However, total foreign production of PCBs was roughly estimated by the Interdepartmental Task Force to be 80-85 million pounds annually prior to 1971. This value included 26 million pounds produced by Japan. Foreign production of PCBs has, however, decreased primarily due to Japanese action on banning the domestic production of PCBs. In 1973 foreign production of PCBs was estimated to be 43 million pounds, accounting for a 50% reduction. Production, trade and use of PCBs by OECD member countries for the year 1973 is given in Table 1.2-1. The combined PCB output of three major European producers, France, Italy and United Kingdom was about 36 million pounds in 1973. World commerce in PCBs is expected to decrease further, due to OECD member countries' activities, and to be essentially confined to capacitor and transformer applications.

1.3 Summary of Recent PCBs and PCTs Imports

A summary of estimated imports of PCBs since 1971 is presented in Table 1.3-1. Importation of PCBs appears to be steady or increasing, and currently is in the range of one percent of the domestic sales reported by Monsanto.

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Table 1.2-1 - Production, Trade and Use of PCBs
OECD Member Countries (1973)

Country	Total Production of PCBs	Total Import of PCBs	Total Export of PCBs	End of Use by Category: Transformer Application	Capacitors (large)	Capacitors (small)	Heat Transfer System	Hydraulic Equipment	Vacuum Pump	Lubricating & Cutting Oil	Plasticizers	Others
Australia												
Austria[2]	*											
Belgium	0	?	?	1.16	0.40	-	?	?	?	?	?	0
Canada	0	2.38	0	1.98[3]	0.44[4]	0.41[4]	0	0	0	0	?	0
Denmark												
Finland	0	0.53	0	0.09[3]	0.44[4]	0	0	0	0	?	0	0
France	21.33	0.66	10.12	6.48	2.87		0.16	0.17	0.01	0.49	1.45	0.25
Germany[2]	*											
Greece												
Iceland												
Ireland												
Italy	5.55	3.53	2.44	2.70	3.14[3,4]	0	0	0	0	0	0.64[4,5]	0.16[6,8]
Japan	0	(2)	(2)									
Luxembourg												
Netherlands	0	?	0	?	?	?	?	?	?	0	0	0
New Zealand	0	0.04[9]	0	0.075	0	0	0	0	0.005	0	0.02	0
Norway[10]	0	0.04	0	0	0.05[4]	0.005	0	0	0	0	0	0
Portugal												
Spain	*											
Sweden[10]	0	0.70	0	0	0.72	0	0	0	0	0	0	0
Switzerland												
Turkey	0	0	0									
United Kingdom	8.97	0.01	6.53	0.71[3]	← 1.82[9] →							
United States	42.18	0.57	8.35	← 37.87[13] →			?	0.04	?	?	0.04[12]	?

Notes:

(1) All quantities are in million pounds

(2) Information is not available

(3) PCB containing 54 wt % chlorine

(4) PCB containing 42 wt % chlorine

(5) PCB containing 64 wt % chlorine

(6) PCB containing 70 wt % chlorine

* indicates PCB producer country

(7) "Others" refers to PCBs were used to reseller and in research

(8) "Others" refers to PCBs used as a fire-retardant in plastics

(9) This figure includes about 6 percent from previously imported material

(10) Amount reported as import and quantities quoted in usage do not agree

(11) With regards to the use of PCBs in transformers and capacitors, definitive figures are not available

(12) Used in investment casting

(13) This figure includes 0.13 million pounds of imported material

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Table 1.3-1

Preliminary Summary of PCBs Import Data for
1971-75 Versus Monsanto Production and Sales Data

	Year or Portion of Year				
	1971	1972	1973	1974	1975
Estimated Imports (lb)	550,000	700,000	480,000	450,000	450,000 (6 mos)
Monsanto Domestic Sales (lb)	34,301,000	26,408,000	37,742,000	34,406,000	7,986,000 (3 mos)
Imports as Percentage of Domestic Sales	1.6	2.7	1.3	1.3	-
Monsanto Exports (lb)	-	6,388,000	8,346,000	5,395,000	1,538,000 (3 mos)
Ratio of Exports to Imports	-	9.1	17.3	13.5	-

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During 1971 and 1972 most of the PCBs imported into the United States originated in Japan, ostensibly corresponding to sales of stocks unsalable in Japan due to pending or established regulatory action. There apparently has been little or no U.S. importation of PCBs from Japan since 1972. The major importer was Marubeni America Corp., West Caldwell, N.J.

Since 1972, most of the imported PCBs originated in Italy, with a small amount imported from France (manufactured by Prodelec). This French material is similar to Aroclor 1242 and is used (40,000-60,000 lb. per year) as a coolant in mining machinery by Joy Mfg. Co., Franklin, Pa. Decachlorobiphenyl (Fenclor DK) is imported from Italy by Yates Mfg. Co., Chicago, Ill., for use in the manufacture of investment casting waxes. Estimated current usage is about 400,000 lb/year.

Polychlorotriphenyls, also used in pattern wax formulations, appear to be imported at an increasing rate. Estimated amounts are:

1973	1974	1975 (6 mos.)
160,000 lb.	330,000 lb.	200,000 lb.

Major importers of PCTs are Progil, Inc. (formerly Prochimie) and Intsel Co., both located in the New York City area. Most of the imported PCTs originate in France (Prodelec).

Use of PCBs and PCTs in casting waxes appears to be generally stable or increasing slowly, and under conditions of lack of regulatory control in the future, such use would be expected to continue at least at the current rate. On the other hand, Joy Mfg. Co. no longer manufactures mining equipment using PCBs as coolant; the amounts imported by Joy are used to service existing equipment. However, since Joy imports only 10 to 20 percent of the total, the overall imports will not be affected greatly by future decreases in imports by Joy.

2.0 FIFTEEN YEAR EXTRAPOLATIONS FOR PCB PRODUCTION AND USE IN ELECTRICAL EQUIPMENT

The subject data base was assembled from domestic sales figures for Aroclors reported by Monsanto – capacitor and transformer sales being summed

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to obtain totals. For certain years (1972-1973), sales data were reported in aggregate, and in such cases, the reported figures were taken as totals, and usage breakdown was accomplished by assigning total amounts of Aroclor 1221 and 1016 to capacitors and total amounts of Aroclor 1242, 1248, 1254, and 1260 to transformers. All 1975 totals were obtained by quadrupling the reported first-quarter sales figures - a process which very likely yields an approximate lower-bound to the actual yearly totals - and, ultimately, Table 2-1 was constructed.

Manifestly, the available data base is far too limited to form the basis for any rational statistical analysis. The strong pertubational decrement in the 1971-1972 interval precludes the application of incremental regression - even if a fifteen-year extrapolation were not required. In short, then, trend analysis becomes a generally risky proposition, and the optimum analytical approach seems to be limited to unbiased extrapolations of least-square linear fits to grouped subsets of the available data points.

Given this, three data base subsets appear promising:

(i.) the full base – using all reported and 1975-estimated data, unweighted and unbiased;

(ii.) a singly-deleted base – using all reported data, but eliminating the 1975 estimates. This tends to weight the extrapolations (however weakly) with regard to recent (last-decade) performance only, but the resulting curves can then be inspected without the bias of the estimated 1975 totals; and

(iii.) triply-deleted base – formed by extracting the depressed 1971 and 1972 totals from the singly-deleted base. This construction eliminated the bias of the 1975 estimates, and discounts the effects of the interval decrements caused by regulatory effects. (A perhaps more realistic picture might be obtained by placing a decremental weight on 1975 totals – under the assumption that some of the roll-back is reactively

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Table 2-1

Total PCB Breakdown by Use
1966 - 1975

Year	Total (10^6 lbs.)	Capacitors (10^6 lbs.)	Transformers (10^6 lbs.)
1966	37.794	28.884	8.910
1967	40.774	29.703	11.071
1968	41.135	29.550	11.585
1969	37.127	25.022	12.105
1970	40.536	26.708	13.828
1971	25.275	14.141	11.134
1972	25.656	20.321	5.335
1973	37.742	23.566	14.176
1974	34.406	22.000	12.000
1975 (est.)	31.944	20.644	11.300

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induced by the strong depression in the 1971-1972 totals. This would result, however, in externally biased extrapolations, and justifying a long-term lag of such effects with the available data appears difficult.)

These data bases, and the unbiased, least-square linear extrapolations derived from them, are graphed in Figure 2-1. Inspection of the curves shows that the 1975 estimate has little effect on the aggregate total; an event readily accounted for by noting that the singly-deleted base has the effect of depressing the capacitor total only slightly more than it elevates the transformer total. The triply-deleted base, however, provides almost no perturbation to the transformer total derived from the full base. Inspection of the curves for the aggregate total and the capacitor total indicate that this arises from the fact that the ratio of their time-derivatives (slopes) for the triply-deleted base is almost equal to its value with the full base.

Generally, the developed extrapolations disagree with mid-1975 industry estimates for the near-term future. Apparently, Monsanto and capacitor manufacturers tend to expect 1975 totals to resemble 1974 totals, followed by a five to ten percent increase in 1976, and a general four to five percent increase over the preceding year for 1977 on. Obviously, increases by a fixed percentage over preceding years yields exponentially increasing totals – an event undoubtedly strongly desired, but probably wholly utopian. Transformer manufacturers appear to tend toward a more conservative view; General Electric for example, expecting the demand for power transformers to rise and the demand for distribution transformers to fall – probably yielding a general saturation of the sales figures when integrated over all types.

Taking the available information into consideration, the impression remains that the triply-deleted data bases probably provide the most likely picture of what might be expected over a 25-year term. Naturally, such scenarios assume the external *status quo* as constant; technological, economic, and regulatory factors being capable of producing strong (and unassessable) variations in usage patterns. As a matter of fact, very recently, Monsanto has publicly announced that they would support a cessation of the PCB production when suitable alternative materials become available.

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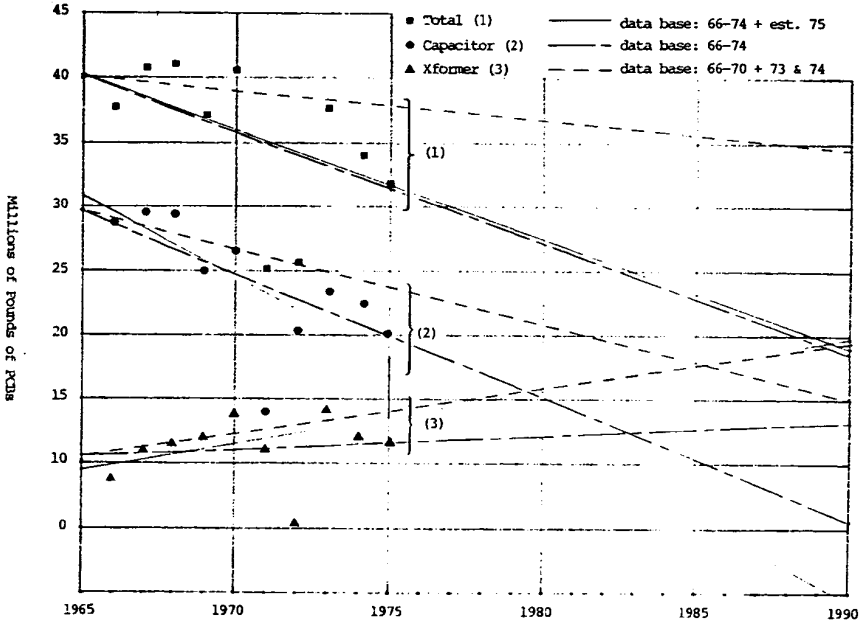
Figure 2-1. Unbiased Extrapolations of Least-Square Linear Curves for PCB Production and Use in Electrical Equipment



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3.0 OVERALL MATERIAL BALANCE

Three separate approaches have been taken to obtaining overall data on total PCBs production, historical usage, and current distribution in the environment. Most of the uncertainty lies in the period 1930-1960, for which Monsanto data are lacking. Use of PCBs in transformers, particularly in electrical distribution systems, apparently began almost simultaneously with commercial production. Extensive use in capacitors can be traced to the intensive development and use of electrical home appliances, starting in the mid to late 1940's. Use in adhesives, paper, lubricants, etc., probably began in the early 1950's, and use of PCBs as a heat transfer fluid began early but increased rapidly between 1950 and 1970.

Using the Monsanto production data for 1960 to 1975, and assuming a linear increase in total PCBs production between 1930 and 1960, we obtain:

Production 1960 - 75	850×10^6 lb
Production 1930 - 60 (30 yr $\times$ 19 $\times$ 10^6lb/yr ave)	570×10^6 lb
Total	$1{,}420 \times 10^6$ lb

Estimates of total PCBs usage by U.S. industries for the period 1930 - 1975 are given below:

PCBs by use category	
Capacitor & transformers	965×10^6 lb
Heat transfer	20×10^6 lb
Hydraulics/lubricants	80×10^6 lb
Misc. industrial	27×10^6 lb
Carbonless copying paper	45×10^6 lb
Other plasticizer uses	115×10^6 lb
Petroleum additives	1×10^6 lb
Total from Monsanto	$1{,}253 \times 10^6$ lb
Estimated total U.S. imports of PCBs	3×10^6 lb
Grant total PCBs usage	$1{,}256 \times 10^6$ lb

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Alternatively, we have fitted least square correlations to each of the sets of Monsanto sales data for various uses, and to the domestic sales data set from 1957 to 1974, projected each plot back to 1930, and integrated. These operations, plus the addition of several other well established data points, produce the following results:

Total Domestic Sales, 1930 - 1970	767×10^6 lb
Domestic Sales, 1971 - 1975	168×10^6 lb
Total Exports, 1963 - 1974	82×10^6 lb
Estimated Exports, 1930 - 1963; 1975	70×10^6 lb
Monsanto In-House Use (unreported as sales)	25×10^6 lb
Total	$1{,}112 \times 10^6$ lb

As a comparison with the above, the 1973 Foster D. Snell study of PCBs concluded that the upper bound of U.S. usage of PCBs over 1934-72 was 1.175×10^9 lb. Adding usage figures for 1973-75 (about 105×10^6 lb), plus 150×10^6 estimated total exports, one obtains:

Estimated Total U.S. Production to Date	1.43×10^9 lb
Estimated Total U.S. Usage to Date	1.28×10^9 lb

Thus, it appears that the approaches taken to obtaining overall production and use quantities from various types of estimates yields:

U.S. Production

Maximum	1.4×10^9 lb
Minimum	1.1×10^9 lb

U.S. Usage

Maximum	1.25×10^9 lb
Minimum	1.0×10^9 lb

Sufficient data have been generated to allow an approach to the usage quantity through estimated quantities now in use or in the environment:

Transformers - 135,000 in service x 2,250 lb/unit average content	300×10^6 lb
Power Capacitors - 5×10^6 in service x 36 lb/unit average content	180×10^6 lb
Industrial Capacitors - 790×10^6 in service x 0.35 lb/unit average content	270×10^6 lb
Total in Electrical Service	750×10^6 lb
Total Other Than Electrical	8×10^6 lb
Grand Total	758×10^6 lb
Estimated "free" PCBs in the environment (see Section IX)	150×10^6 to 175×10^6 lb
Estimated amount degraded or incinerated (20×10^6 lb. by contract incineration; 5×10^6 lb incinerated with sewage sludge and other solid wastes; and 30×10^6 lb degraded mono and dichloro homologs) -	55×10^6 lb

Estimated amounts to landfill or dump:

Ten percent of capacitor and transformer usage as production wastes - $1.06 \times 10^9 \times 0.10$ =	110×10^6 lb
Obsolete electrical equipment (capacitors mainly) -	80×10^6 lb
Other sources (paper, plastics, etc.) -	100×10^6 lb
Estimated total	290×10^6 lb

In summary:

Amount in use	758×10^6 lb
Amount in landfills	290×10^6 lb
Amount "free" in soil, water, air, sediment	150×10^6 lb
Amount degraded or incinerated	55×10^6 lb
Total	$1,253 \times 10^6$ lb

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Thus, using estimates, we can account for the maximum usage of 1.25×10^9lb. calculated previously. We believe that the ranges of production and usage are well-defined by the maximum and minimum values presented above, and that the accuracy of the maximum values are sufficient for use in gross calculations pertaining to the PCBs problem.

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SECTION VIII

SUBSTITUTES FOR PCBs

1.0 INTRODUCTION

In 1970, the Monsanto Company announced a voluntary restriction on sales of PCBs for all but closed electrical applications. As a result of this action, since 1972 the use of domestically produced PCBs has been limited to the manufacture of electrical capacitors and the manufacture and maintenance of electrical transformers.

Satisfactory substitutes have been developed for all of the other previous uses of PCBs except in the manufacture of investment casting wax. Imported PCBs have been the sole source of material for this application. There are no complete data available on imports; however current aggregate information indicates that PCB imports are about one percent of domestic production.

A number of materials are currently being developed as substitutes for PCBs. The replacement of PCBs by any of these materials will depend on the specific technological, economic, and institutional requirements which govern each specific application. The evaluation of the substitutes must be based on careful consideration of all of these factors as they apply to each specific application where PCBs are currently being used.

2.0 ELECTRICAL CAPACITORS

An electrical capacitor is a device which stores electrical energy when a voltage differential is applied across the device. This stored energy reappears in the circuit as the voltage is decreased. The capacitor therefore performs an electrical function equivalent to that of a spring in a mechanical system. The amount of electric charge (q) which a specific capacitor can store

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is a function of its size, or capacitance (c), and the voltage (v)

$$q = cv \tag{1}$$

and the energy stored in the capacitor (w) is a function of the capacitance and the square of the voltage:

$$w = \tfrac{1}{2}cv^2 \tag{2}$$

This energy is stored in the capacitor in the form of an electric field and in the dielectric material which is exposed to that field.

2.1 Function of the Dielectric Material

When a material is placed within an electric field there is a tendency for the charges associated with the constituent molecules of the material to move in the direction of the field (the positive charges move in the direction of the applied field, the negative charges in the opposite direction). If the material is a conductor, the mobile charges, usually electrons, will move freely under the influence of the field and a current is said to flow. However, if the material is a non-conductor, the applied electric field will cause a spatial displacement of the charge centers of the constituent molecules, with the result that surface charges will be induced on the material. The charge on opposite faces of the material will be opposite in sign and will generate an electric field within the material opposing the applied field. Such a material is known as a dielectric and is characterized by a parameter defined as the ratio of the electric field that would exist in that space if the medium were replaced by vacuum to that actually found within the dielectric - this parameter is referred to as the dielectric constant. The dielectric constant of most materials, at least at low frequencies, is greater than unity.

Since the effect of an applied electric field on a dielectric medium is the generation of a surface charge, it is clear that work must be done in the separation of these charges. Clearly, the larger the applied electric field, the larger the surface charge, and conversely, when the electric field is removed, the surface charge is zero. The energy that is required to establish the necessary surface charge is stored within the dielectric and can in most cases be recovered without loss by removing the external electric field.

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In practice, the external electric field is established by applying electrical charges to a pair of metal plates placed on the opposite surfaces of the dielectric. Although the geometry of the conductor-dielectric sandwich can take a wide variety of forms, the specific geometry that is of most interest is that in which conductors are parallel plates separated by the dielectric. In this case the capacitance of the device is given as

$$C \propto \frac{eA}{d} \tag{3}$$

where e is the dielectric constant, A the area of each plate and d the spacing (the thickness of the dielectric).

As is stated above, the magnitude of the surface charges that are formed on the dielectric increases as the applied electric field increases. Eventually, the external electric field may become sufficiently strong to rupture the bonds that hold together the charges on the individual constituent molecules with the result that the dielectric breaks down; i.e., conducts current. The critical voltage (V_c) for a specific capacitor is

$$V_c = E_c d \tag{4}$$

where E_c is the dielectric strength, i.e. the maximum potential gradient (voltage) that the dielectric can sustain without rupture. Clearly, the dielectric constant and the critical voltage, or dielectric strength, are essentially unrelated.

The critical voltage of the dielectric material can impose severe limitations on the maximum voltage at which a capacitor can operate. The electric field strength in a capacitor is strongest at sharp edges and points caused by surface roughness and the edges of the conductive plates. If the electric field at these points exceeds the critical voltage of the dielectric, a corona discharge can occur which results in current leakage and heating of the capacitor and causes chemical degradation of the dielectric material. This critical voltage for corona discharge depends on both the geometry of the capacitor and the properties of the dielectric, and is known as the corona inception voltage. Air has a rather low dielectric strength; the presence of air bubbles in the dielectric will result in corona discharges if the capacitor is operated at applied voltages above about 270 volts.

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When several capacitors, say C_1 and C_2, are connected in parallel, then the voltage across each is the same, V, while the charge on the capacitors is $Q_1 = C_1V$ and $Q_2 = C_2V$; hence the capacitance of the parallel combination is given as

$$C_t = C_1 + C_2 \tag{5}$$

On the other hand, if the two capacitors were connected in series, then the charge, Q, would be the same for each. In this case, the respective potentials would be given as $V_1 = Q/C_1$ and $V_2 = Q/C_2$, with the result that the total capacitance is given as

$$1/C_t = 1/C_1 + 1/C_2 \tag{6}$$

From the above considerations it can be seen that the effect of a small hole through the dielectric will be to produce a very small reduction in the overall capacitance, since the resulting structure may be considered as two capacitors, one with the normal dielectric, the other with air dielectric, in parallel. On the other hand, the breakdown strength of air is considerably less than that of most practical dielectric materials, so that the effect of such a discontinuity in the dielectric will primarily be in reducing the critical voltage of the resulting structure.

On the other hand, the effect of a gap between the dielectric and the plates is more serious since the resulting structure will act as if it were made up of several capacitors in series. From Eq. (6), it can be seen that the smallest capacitor in a series circuit will determine the total capacitance of the structure. Thus, a gap between the plates and the dielectric will have the effect of reducing the capacitance without a reduction in the dielectric strength.

In most practical devices, the assumption that the sole effect of the dielectric is the reduction of the internal electric field by the induction of surface charges is not entirely correct. In all such practical cases, there is a leakage current that flows through the dielectric. This leakage current produces heat within the dielectric. This leakage is very small in useful dielectrics, but the heating effect is not always

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negligible. An additional dissipative process results when the dipole moment induced within the molecules of the dielectric is not exactly in phase with the inducing electric field. In those cases where in the constituent molecules have a permanent dipole moment, i.e. water, the inability of the orientation processes to follow the changes in the applied field becomes the dominant energy dissipation process; this is the basis of dielectric heating.

The combination of the mechanism by which energy is dissipated within the dielectric is called the loss-tangent; the smaller the loss-tangent, the smaller the energy loss within the dielectric and hence the better the capacitor.

2.2 Practical Capacitors

In its simplest form, a capacitor is a pair of metal plates separated by a dielectric material. Depending on the application, a great variety of structures have been used ranging from parallel plate mica or glass dielectrics for very small capacitors, through tantalum-tantalum oxide-tantalum structures which have very large capacitances with very low operating voltage ratings. The capacitors which use PCBs as the dielectric material have capacitance values in the range of a few tenths to tens of microfarads and are usually spiral wound of two thin aluminum foils and two paper spacers. To illustrate the utility of spiral winding, a 0.5 mfd capacitor made of two layers of aluminum foil 2.5 inches wide by 0.0005 inches thick and alternate layers of paper (dielectric constant = 2) 0.001 inches thick, would have a diameter of only 0.9 inches, whereas, in the plane parallel configuration, the structure would be 2.5 inches by 220 inches. Incidentally, taking the dielectric strength of the paper to be of the order of 500 kv/cm, the voltage rating of the above example capacitor would be about 1250 volts.

The manufacturer of spiral would metal/paper capacitors must avoid the presence of small imperfections in the paper dielectric and must insure complete and reliable matching of the metal foils to the surfaces of the paper. As an alternative to the requirement of very high quality control of the paper and of the forming process, it has been found to be cost effective to evacuate the spaces within the wound capacitor and to subsequently fill

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the voids with a suitable liquid dielectric material prior to sealing the completed unit. This liquid displaces any air which may be left in the capacitor, thereby raising both the dielectric constant and the critical corona inception voltage.

2.3 Required Properties of Dielectric Liquid

The properties that are essential for the liquid dielectric can be described in terms of the functions that the liquid must fulfill:

- Electrical Properties - Should have a dielectric constant at least as large as that of the solid dielectric spacer, and a dielectric strength at least as high as that of the solid dielectric. The liquid must have a low loss factor to assure electrical efficiency and a high resistance to the formation of corona discharges.
- Physical Properties - Must be liquid at a suitable temperature to allow processing of the capacitor. Further, it should be liquid over the operating temperature range of the resulting capacitor with a sufficiently small coefficient of thermal expansion so as to fulfill its function over the entire temperature range. Must have a boiling point sufficiently elevated to ensure that the vapor pressure at the maximum operating temperature of the capacitor does not cause rupture of the container.
- Chemical Properties - Must be chemically compatible with the solid dielectric material and with the metal plates. Specifically, the dielectric liquid must wet both the plates and the solid dielectric without altering either material chemically or physically over the entire operating temperature range. The dielectric liquid must also be chemically stable at elevated temperatures and in the presence of intense electric fields so that its properties do not change over time.

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- Flammability - Should be non-flammable and produce no flammable breakdown products if electrical arcing occurs within the capacitor.
- Cost and Availability - Should be inexpensive and readily available with well defined and standardized properties.
- Toxicity - Should be non-toxic and its possible breakdown products should be non-toxic.
- Environmental Persistence - Should be environmentally degradable and non-bioaccumulating.
- Legislative Acceptability - Must be acceptable under the laws of the U.S. and of all other countries to which capacitors are exported. Should be acceptable under the relevant electrical codes which govern the use of capacitors.

2.4 The Use of PCBs in Capacitors

PCBs have been the standard dielectric liquid used in almost all liquid-filled capacitors since 1929. Prior to 1952 the liquid used in capacitors was Aroclor 1254 (54 percent chlorine); it was then replaced by Aroclor 1242 (42 percent chlorine), which has better electrical properties. In September 1971, Monsanto introduced a new capacitor liquid, Aroclor MCS-1016, which is a modified Aroclor 1242. This material is the standard against which the properties of any other proposed capacitor dielectric fluid must be compared.

2.4.1 Properties of PCB Capacitor Dielectric Liquid[1]

The relevant properties of Aroclor 1016 are as follows:

- Electrical Properties

dielectric constant (ASTM D-150-47T)	5.85 ($25^{o}C$)
dielectric strength (ASTM D-149-44)	>35 KV
resistivity (ASTM D-257-46)	$>500 \times 10^{9}$
loss-tangent (Dissipation factor-ASTM D-150-47T)	0.0025

- Physical Properties

melting point (pour point)	-19°C
viscosity at 100°F	71-81 SUS
boiling point	325-366°C
specific gravity (25°C)	1.362
coefficient of thermal expansion	.00068 cc/cc°C

- Chemical Properties

corrosiveness: liquid - noncorrosive
breakdown products - corrosive

solvency: high, but satisfactory materials have been developed

stability (max. service temp.) 95°C

- Flammability

liquid (Cleveland open cup flash point): 141°C

breakdown products: nonflammable (primarily HCl and carbon)

- Cost and Availability

cost $5.14/gallon

availability - no problem

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. Persistance

environmental - very persistent

% biodegradation (48 hour activated sludge) $33 \pm 15\%$[2]

bioaccumulating - very

. Legislative Acceptability

banned in Japan, essentially banned in Sweden

2.4.2 Advantages and Disadvantages of PCBs in Capacitors

Aroclor 1016 has a relatively high dielectric constant of 5.85 which is well matched to the dielectric constant of 6.10 of the paper used in capacitors. This mixture of PCBs is chemically very stable, even in the presence of high temperatures and intense electrical fields. It is probable that some slight dechlorination of the PCB occurs during the long term operation of capacitors. The resulting HCl would lower the dielectric strength of the PCB. However, the Aroclor 1016 used in capacitors usually contains a few tenths of one percent of a chemical scavenger (usually an organic epoxide) which reacts with any HCl which is formed, and thereby extends the life of the capacitor.

The only major problems associated with the use of PCBs are their extreme environmental persistence and chronic toxic properties which are made more severe by the high degree of bioaccumulation which occurs in the environment. The recent restrictions imposed by the governments of Japan and Sweden on the use of PCBs in those countries will require that a suitable substance be developed for use in electrical equipment which will be exported.

2.4.3 Usage of PCBs in Capacitors

The General Electric Co. reports that approximately 100 million PCB type capacitors are produced annually in the U.S. with a value of 140 million dollars, most of them for first-time use.[3] Total annual PCB requirement for capacitor manufacturing is 21 million pounds, about 50 percent of which is used in large power factor correction capacitors.

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Capacitors used in lighting and air conditioning applications contain 0.005 to 0.09 gals. (0.05 to 1.0 lbs.) of PCBs. The largest power capacitors contain about 6.7 gals. (77 lbs.) of PCBs. The most popular size contains about 3.1 (36 lbs.). The National Electrical Code requires that any installation of capacitors in which any single unit contains more than 3 gallons of combustible liquid shall be in a vault like that required for transformers.[4]

The life expectancy of capacitors exceeds 10 years for lighting applications and more than 20 years in electric utility power transmission application. Although capacitors are considered long-lived products, they could fail due to poor process control, materials quality and misapplication. According to G.E., existing PCB capacitors have been developed to the point that failures are considered essentially negligible. In each application, the first-year failure rates are less than 0.2 percent. This level of life and reliability had not been achieved prior to the introduction of PCBs. Furthermore, the relative non-flammability of askarels significantly reduces the fire hazard that might otherwise accompany those failures that result in rupture of the case. Capacitors are not rebuilt and returned to service after failure. They are disposed of and replaced by new capacitors.

2.5 Alternatives to the Use of PCBs in Capacitors

There are two main approaches that might be adopted in the development of substitutes for the PCBs in capacitor applications, (a) a straightforward replacement of PCBs that would require minimal alternation of the present production techniques; and (b) the introduction of new production techniques designed to eliminate the need for a liquid dielectric. In either case, the alternative solution must be significantly less environmentally distressing than the currently used PCBs.

2.5.1 Substitutes for PCBs

So long as the present method of construction of capacitors is used, the dielectric liquid is required and must necessarily satisfy the physical, chemical, and toxicity requirements at least as well as do PCBs. These requirements can be relaxed only in conjunction with a more or less severe restriction on the maximum operating temperature of the capacitor. On the other hand, some sacrifice in the dielectric constant and dielectric

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strength would be possible by increasing the dimensions of the capacitors. In many applications this increased size would be troublesome, but not so serious as to be impractical. Further, there are some applications in which the non-flammability of the dielectric liquid and of its possible breakdown products could be somewhat sacrificed. Finally, the cost factor could be considerably relaxed.

A number of compounds are being developed as replacements for PCBs in capacitors. The following list of compounds must all be considered as possible substitutes for PCBs in at least limited applications.

2.5.1.1 Phthalate Esters:

2.5.1.1.1 Dioctyl Phthalate: (DOP)

Current status:
Used in capacitors in Japan. Used by General Electric Co. under the trade name "Econol" in capacitors manufactured for export to Japan.

Advantages:
Price: one-half that of PCB.
Availability: Widely used as a plasticizer for PVC.
Dielectric Constant: 5.3; similar to PCB.

Disadvantages:
Chemical stability: capacitors are limited to 85°C max. vs 95°C max. for PCB.
Corona inception voltage: lower than PCB.(5)
Flammability: Flash point is relatively high (220°C) but more flammable than PCBs.
Toxicity: Suspected carcinogen. Extensive additional testing is required.(5)

2.5.1.1.2 Diisononyl Phthlate:

Current status:
Currently being tested by Exxon Chemical under the trade name "Enjay 2065".(6)

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Advantages:

Dielectric Constant: Similar to DOP.

Availability: Can be made by a modification of the DOP manufacturing process.

Chemical stability: Better than DOP.

Disadvantages:

Availability: Not currently available in large quantities.

Flammability: Better than DOP, but more flammable than PCB.

Toxicity: Should be similar to DOP.

2.5.1.2 Alkylated PCB

2.5.1.2.1 Isopropyl Dichlorobiphenyl

Current status:

Being test marketed in Europe by Prodelec under the trade name "Chloralkylene".[7]

Advantages:

Electrical properties: Can be used as a direct substitute for PCBs.

Bioconcentration: Less concentrated in food chain than PCB.

Biodegradation: More degradable than PCB.

Disadvantages:

Cost: Twice that of PCB, resulting in a 5% to 10% increase in the cost of capacitors.

Flammability: More flammable than PCB.

Toxicity: Acute toxicity ½ that of trichlorobiphenyl, chronic toxicity has not yet been fully investigated.

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2.5.1.3 Alkylated Chlorodiphenyl Oxide

2.5.1.3.1 Monobutyl Monochlorodiphenyl Oxide

Current status:

Being marketed by Dow Chemical Co. under the trade name "XFS-4169L".[3] Undergoing long term service tests in capacitors by McGraw-Edison Co.

Advantages:

Electrical Properties: Loss-tangent lower than PCB.[9] Corona inception voltage higher than PCB.[9]

Biodegradation: Three times as degradable as PCB.

Bioconcentration: Less than one-tenth that of PCBs. One-twenty second that of PCB in 90-day rat feeding test.

Acute toxicity: LD_{50} = 10 gm/kg vs 1.6 gm/kg for PCB. Does not irritate rabbit skin or cause chloracne.

Disadvantages:

Electrical properties: Dielectric constant is somewhat lower than that of PCB (4.5 vs 5.85) which will require a larger plate area for a given capacitance.

Availability: Currently not available in large quantities. Two to three years would be required to build sufficient manufacturing capacity to supply the capacitor industry.

Cost: Likely to be higher than PCB.

Flammability: Somewhat more flammable than PCB; flash point = 104°C.[9]

Chronic toxicity: Reported to be not mutagenic in the Ames test. Long term tests of the toxicity of biodegradation products have not been reported. It is suspected that highly toxic dioxins may be formed as a degradation product,[7] sp extremely careful long term testing will be required to prove the environmental safety of this compound.

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2.5.1.4 Silicones

Current status: Developmental work is being done in the U.S. by Dow Corning Co. No information is currently available, but Dow Corning has indicated that a formal announcement will be made late in 1976.[10]

2.5.1.5 Diaryl Sulfone

Current status: The Monsanto Company has been conducting extensive tests with a proprietary dielectric liquid trade named "MCS-1238".[2] Detailed chemical information is not currently available on this material; however, an example cited in German and U.S. patent disclosures is a mixture of tolylxylyl sulfone, isopropyl biphenyl, and minor ingredients which may be antioxidants. Complete information has been promised by Monsanto for the late first quarter of 1976.

Advantages: (MCS-1238)
Dielectric constant: 6.0
Corona inception voltage: similar to PCB.
Biodegradation (48 hour activated sludge): 70% ± 10%.
Bioaccumulation: does not concentrate in food chain.
Toxicity: Rat oral LD_{50} = 3.8 g/kg. Rabbit dermal LD_{50} - 5 to 8 g/kg.

Disadvantages: (MCS-1238)
Flammability: more flammable than PCBs.
Chronic toxicity: lack of data.

2.5.2 Elimination of Dielectric Liquids in Capacitors

Because of the complex and strongly interacting requirements on a liquid dielectric material, there is considerable interest in the development of capacitor designs which do not require a liquid dielectric. The rather advanced technology involved in the production of very thin plastic films of very high physical integrity, such as is required in many food packaging applications, has opened the way for the production of plastic

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films of suitable dielectric constant and dielectric strength for capacitor applications. The parallel development of methods for the deposition of thin, carefully controlled metallic films on non-conducting surfaces, such as is widely practiced in the semiconductor industry, suggests that the use of a liquid dielectric material could be circumvented by metallic films deposited onto suitable plastic substrates. The resulting metallized film can be spirally wound into useful capacitors. The essential problems associated with this approach, aside from the development of suitable high speed processing equipment, lie in the selection of a plastic substrate that is tractable but also stable at sufficiently high operating temperatures, and in the complete elimination of air from the capacitor. An additional problem with this approach lies in the nature of the polymers that have been studied; nearly all of the suitable materials are themselves flammable and so are their probable breakdown products.

A number of different plastic films are used in low voltage DC capacitors. Most of these materials exhibit a relatively high loss-tangent (dissipation factor) which results in over-heating when subjected to an alternating electric field. Only polypropylene has a loss-tangent sufficiently low so that it can be used in AC capacitors, and the dielectric constant of this material is about 2.2 (vs 5.85 for PCB).

The polypropylene film that is used in capacitors is considerably thinner than that used for packaging and decorative applications. There is no current source of satisfactory capacitor grade polypropylene film in the U.S. The technology for metallized polypropylene film capacitors comes from Pyè TMC of England which is partially owned by Philips. Representatives of this company have approached most major U.S. manufacturers. Currently, this technology has been purchased by one U.S. manufacturer at a cost of four percent of their capacitor sales for the life of the technology usage. The failure rate of the dry film capacitors is reported to be 20 times that of PCB filled capacitors, primarily due to corona discharges into air that is trapped in the dielectric layers. Present efforts on dry film type capacitors are directed toward the development of a suitable capacitor design. Polypropylene capacitors are widely used in Europe at voltages up to 250 volts. Capacitors suitable for U.S. applications are not expected for 3 to 5 years.

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2.6 The Use of PCB Capacitors in Electrical Equipment

Each of the specific uses of PCB capacitors imposes special requirements on the performance of the capacitor and on the properties of the dielectric liquid. The evaluation of the various substitute liquid dielectrics and of the dry capacitor designs must be based on the suitability of the resulting capacitors for each of these uses.

2.6.1 Power Factor Correction

The largest use of PCB filled capacitors is to increase the efficiency of electrical power distribution by correcting for the power factor of inductive machinery such as industrial motors, induction furnaces, and fluorescent light transformers. In general, the load imposed on a power line by these electrical devices is not purely resistive, but is also partly inductive. The voltage drop (V_L) across such an inductor is proportional to the rate of change of current through the device; hence

$$V_L = -L \frac{di}{dt} \tag{7}$$

where the negative sign expresses the reaction of the inductance (L) to a change in current (i) through the inductance. If the current is expressed in the form

$$i = i_o e^{j\omega t} \tag{8}$$

where $j \equiv \sqrt{-1}$, $e^{j\omega t} = (\cos \omega t - j \sin \omega t)$, $\omega = 2\pi f$, $f \equiv$ frequency.

Then

$$V_L = j\omega L \, i = Z_L \, i \tag{9}$$

where Z_L is the inductive reactance given by

$$Z_L = j\omega L \, . \tag{10}$$

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On the other hand, for a capacitance (C), the potential difference

$$V_C = \frac{Q}{C} = \frac{\int i\,dt}{C} = -\frac{1}{j\omega C}\ i \tag{11}$$

where Q is the electric charge on the plates of the capacitor. Hence, the capacitive reactance Z_C is given by

$$Z_C \equiv -\frac{1}{j\omega C}\ . \tag{12}$$

If a series circuit containing inductive (L), capacitive (C), and resistive (R) elements has a potential difference $v = v_o e^{j\omega t}$ across it, the relation between current and applied potential difference is given by

$$Ri + L\frac{di}{dt} + \frac{1}{C}\int i\,dt = V_o e^{j\omega t} \tag{13}$$

A solution of this equation is in the form

$$i = i_o e^{j(\omega t + \theta)} \tag{14}$$

where θ is the phase difference between the applied potential difference and the resulting series circuit current. On substitution of the assumed solution into the differential equation (13), one finds

$$\left(j\omega L + R - \frac{j}{\omega C}\right) i = V \tag{15}$$

which is, in the general (Ohm's Law) form,

$$Z\,i = V \tag{16}$$

where

$$Z \equiv R + j\left(\omega L - \frac{1}{\omega C}\right) = |Z|\ e^{j\phi} \tag{16'}$$

where

$$|Z| \equiv \sqrt{R^2 + \left(\omega L - \frac{1}{\omega C}\right)^2} \tag{16''}$$

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and

$$\phi = \tan^{-1}\left(\frac{\omega L - \frac{1}{\omega C}}{R}\right) \qquad (16''')$$

and, in order to satisfy Eq. (16)

$$\theta = -\phi \ . \qquad (17)$$

The power dissipated in a series R, L, c circuit is given by

$$P = \frac{1}{T}\int_{0}^{T} VI \, dt \qquad (18)$$

where T is the period $\equiv \frac{1}{f}$

which, on integration, yields

$$P = I_o V_o \cos\phi \qquad (19)$$

where ϕ is the phase angle given by Eq. (16'''').

The importance of the phase angle is best described by noting that electrical power is generated in such a manner that the voltage and current are in phase, i.e. $(\cos\phi)_{generation} \equiv 0$.

Hence

Power generated - power consumed = Power losses in transmission

$$V_o I_o - V_o I_o \cos\theta = V_o I_o (1 - \cos\theta) = \text{power loss due to unfavorable phase angle} \qquad (20)$$

Since the voltage is fixed and $\cos\theta \leq 1$, the transmission line current must be increased in order to supply the load when there is a lagging phase angle. However, the resistive losses in the transmission lines are proportional to the square of the current transmitted. Therefore,

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efficient transmission of electrical energy requires that the net phase angle, or power factor, of the load be as close to unity as possible. This power factor correction is achieved by the introduction of a capacitor in series with the inductive load at the load end of the line.

The function of a capacitor in such a circuit can perhaps be better understood by examining the interchange of electrical energy among the various components of the circuit. In an inductive device, such as a motor or a fluorescent light, which is subjected to an alternating current, a considerable amount of energy is stored in the form of a magnetic field and then returned to the circuit in the form of current when the voltage decreases. In a purely inductive circuit, this current is transmitted back to the generator and is lost in the form of heat in the transmission lines. The energy required to form the magnetic field during the next cycle must then be supplied by the generator. If a capacitor is placed in the circuit near the inductive load, the energy from the collapse of the magnetic field is stored in the capacitor in the form of an electric field when the voltage decreases, and then is transferred back from the capacitor to the inductive device to reform the magnetic field during the next cycle. Since the energy to form the magnetic field is transferred between the capacitor and the inductive device, it does not appear in the transmission lines. This decreases both the heat losses in the transmission lines and the amount of energy required from the generator.

The capacitor used for power factor correction functions as a temporary storage device for electrical energy. It is important that the energy losses be minimized, implying a low loss-tangent for the capacitor and a minimum distance between the capacitor and the inductive device. The other physical and electrical properties of the capacitor are a function of the particular application. There are three general types of power factor correction capacitors: high voltage power, low voltage power, and lighting ballast capacitors.

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2.6.1.1 High Voltage Power Factor Capacitors

Power factor correction can be furnished by the electric utility by installing capacitors at substation locations. These capacitors are designed to operate at high voltages of 4800 to 13800 volts, and are manufactured in a size range from 15 kvar to 200 kvar. Each capacitor contains about 2 to 2½ gallons of PCBs, most of which is trapped in the porosity of the paper dielectric. These capacitors are generally installed in banks in a substation or mounted in groups on utility poles.

The failure rate of high voltage power factor capacitors is approximately .3% per year. These capacitors are usually protected by fuses so that the failure of one capacitor in a bank will not cause failure of other capacitors. Rupturing of these capacitors on failure is relatively unusual, and even when the case does rupture, loss of PCB is generally less than ½-gallon as most of the liquid is absorbed by the paper in the capacitor.

The high voltage power factor capacitors are usually installed outdoors in non-hazardous locations. Fire resistance is therefore of minor importance. The dielectric must have a high dielectric constant and a high resistance to corona formation in order to operate successfully at high voltages.

2.6.1.2 Low Voltage Power Factor Capacitors:

Electrical utilities structure their rates so that there is an economic advantage to the industrial user to supply the power factor correction for major inductive loads such as motors, induction furnaces, and welding machines. The capacitors for these applications are designed to operate at 250 to 575 volts.

The PCB/paper combination used as the dielectric in spiral wound capacitors operates most efficiently at a voltage of 400 volts per mil. Technological limits on paper manufacturing limit this dielectric combination to a minimum thickness of about one mil, so the full efficiency of these capacitors is not achieved at voltages below 400 volts. However,

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capacitors of this type are used for power factor correction for voltage applications down to 220 volts with the motors in heavy duty whole-house air conditioners.

Low voltage capacitors are usually built into the equipment or located close to the inductive machinery in manufacturing plants. Important requirements of the dielectric and low flammability, low toxicity of the liquid and its degradation products, are chemical stability to achieve long service life of the capacitors. Dry film capacitors could find considerable use in 220 volt applications where space is not a severe limiting factor, as in air conditioners.

2.6.1.3 Lighting Ballast Capacitors

Normal fluorescent light fixtures are designed to operate on 110 volt power circuits. The fluorescent bulbs, however, require about 300 volts to operate. This high voltage is supplied by a transformer which is built into the fixture. A small percentage of fluorescent lights are built with a coil-and-core transformer and no power factor correction. These units are sold for household use on the basis of low initial price. The power factor of these lights is about 0.7.

The fluorescent lights which are manufactured for commercial and industrial applications all have the high voltage supplied by a ballast. This ballast consists of an auto transformer connected in series with a 4μf capacitor. The capacitor is of foil-PCB-paper construction and is sealed into an aluminum can. The transformer and capacitor are packaged in a steel can which is filled with a mixture of asphalt and sand as a potting compound. This finished ballast is about 1" x 2½" x 12", and has a life expectancy of 10 to 15 years in normal service. The lighting fixtures using this arrangement have a power factor of about 0.9. The capacitor in a fluorescent light ballast is usually installed very close to the bulbs, and depending on the design of the fixtures, the ballast operates at temperatures of 85 to 90°C.

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High efficiency mercury arc and sodium arc lights are widely used for highway lighting and other high-intensity applications. The ballast units which supply the high voltage for these lights are similar to those used in fluorescent lighting, except they supply more power at a higher voltage.

It should be remembered that the amount of energy that can be stored in a capacitor is proportional to the square of the voltage, so that a 110 volt capacitor would require 8 times the plate area of a capacitor operating at 300 volts.

The major requirements for ballast capacitors are:

small size, implying a high dielectric constant;

ability to operate at 300 volts, which implies a complete exclusion of air so as to avoid corona discharge problems;

chemical stability when exposed to 90°C for long periods of time; and

non-flammability because of the use of the ballasts in houses and other flammable, hazardous locations.

Aerovox reports that they are developing a dry type metallized polypropylene capacitor which could be used in fluorescent ballast applications and that this design would be good for industrial applications up to 370 volts.(11) Application of these units up to 440 volts is considered a possibility. This substitute, when available, would be suitable for 50 percent of the current capacitor applications. It would increase the cost of low voltage power factor capacitors by 20 percent as compared to a PCB unit but would double the cost of ballasts (separate units would be required for purposes of start and storage). The film and metallizing equipment used in these capacitors are manufactured in Europe and currently must be imported. The use of this technology will require major redesign of the parent products, particularly when used in fluorescent light ballasts and room size air conditioners. Because of space and temperature limitations, the dry film capacitors could not generally be used to replace failed capacitors in existing electrical equipment.

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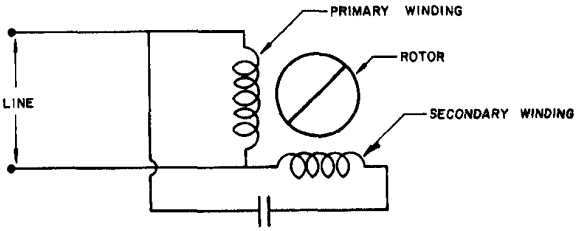
It should be noted that the general use of dry film capacitors in European fluorescent lights is not comparable with U.S. practice. The European line voltage is normally 250 volts, which is below the corona discharge voltage into air, but which allows a decrease in size of the capacitor by a factor of 6 compared to 110 volt applications. In addition, the European fixtures are usually single bulb, rather than the dual bulb fixtures used in the U.S., and the auto transformer is much less reactive as it needs only to increase the voltage from 250 to 300 volts. As a result, much less capacitance is required for power factor correction in European fixtures, and the capacitor, can operate efficiently at normal line voltages. Finally, the capacitors in European fluorescent fixtures are installed as discrete components to allow for their replacement; this is necessary because of the higher failure rate of dry film capacitors compared to U.S. capacitors.

In spite of the relative severity of the technical requirements for U.S. ballast capacitors, industry sources indicate that there is probably a 50 percent chance that a usable dry film capacitor will be available in the U.S. by the end of 1976.

2.6.2 Motor Starting Circuits

Electric motors for residential use are designed to operate on single phase current. A number of different methods are used to develop the rotating magnetic field that is required to start the motor, and these methods differ in the amount of torque that is developed at low speeds. Certain applications, particularly compressors in air conditioning units, require a very high starting torque. This is achieved in a single phase motor through the use of a capacitive starting circuit.

In a capacitor run motor, stator windings are connected as shown below:



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The starting field is connected to the power supply through a capacitor; the result is a starting winding current which leads the applied voltage. Hence, at standstill, the rotor sees fields nearly 90° apart in time as well as 90° apart in space. The resulting, effectively rotating, field results in high starting torque and a high power factor (important during the period when the back emf due to rotor motion is low so that the starting current is significantly higher than the running current). Because of the inductive effect of the starting winding, the capacitor is subjected to a voltage substantially higher than the line voltage. Most 110 volt appliance motors are designed so that the capacitor operates at an effective voltage of 370 volts, thus making optimum use of the characteristics of foil-PCB-paper capacitors.

The capacitor not only performs the necessary function of generating the starting field, but also provides significant power factor correction. In larger motors – primarily 220 volt air conditioner motors – the PCB motor run capacitor is sized for optimum power factor correction and additional capacitance is provided during the first few seconds of start-up by an electrolytic capacitor in parallel with the PCB capacitor. The electrolytic capacitors provide very high capacitance in a small package, but they have a dissipation factor of about 7 percent which causes rapid temperature increases. The electrolytic capacitor is disconnected by a centrifugal switch when the motor reaches running speed. This prevents failure from overheating and results in a configuration with good operating characteristics and satisfactory power factor.

The motor run capacitor is normally built into the motor. This results in a requirement for small size, long life, and fire safety for the capacitor. It is possible that dry film capacitors could be used in this application. However, the high voltages suggest that a liquid dielectric capacitor would be more suitable if a satisfactory substitute were developed for PCBs.

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In some applications, DC motors can be used in place of single phase AC motors. Such DC motors are used in some European electrical appliances where the electronic speed control that can be achieved with the DC motor results in a savings compared to the more complex speed control mechanisms required with an AC motor. In these European appliances, the DC power is supplied by a silicon rectifier. However, the output from the rectifier must be filtered to eliminate the AC components, and this filter circuit normally uses a liquid filled capacitor. In addition, the DC speed control circuit requires an additional capacitor. While these circuits could be redesigned to eliminate the use of capacitors, the resulting DC motor would not appear to be economically competitive with the capacitor run motor except in a limited number of special applications.

2.6.3 Electronic Filter Capacitors

Rectifier circuits are used to supply DC current to electronic components. For instance, the circuitry of most U.S. television sets operates at 300 volts DC. The output of the rectifier must be filtered to achieve a stable DC current. Most television sets use a PCB capacitor operating at 300 volts to pass the AC components of the current. This achieves the required 300 volt DC power required by the other components.

Requirements for this capacitor are long life at 300 volts, small size, and good fire resistance. Either a dry film capacitor or a suitable liquid dielectric capacitor could be substituted for the PCB capacitor in this application, although the larger size of the dry film capacitor may limit its use in repairing existing television sets.

2.7 Institutional Barriers to Substitutes for PCBs in Capacitors

The final choice of an acceptable substitute for PCBs will be made by the capacitor manufacturers based on the performance characteristics and fire safety of alternate dielectric materials. This choice will be affected by performance warranties that are common in this industry and by evaluations of safety as reflected in the codes and regulations which govern the use of capacitors. The traditional industry practices and the formal regulations both impose institutional barriers to the acceptance of a substitute for PCBs.

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These barriers are a major factor in the rapid replacement of PCBs, and should be carefully considered in the formulation of government regulations and in the industrial marketing of alternate dielectric materials.

2.7.1 Performance Acceptability

Capacitors are sold with stringent performance warantees which cover both the capacitance and the expected life or maximum failure rate of the capacitors. These warantees are based on various capacitor standards which are established by industry groups. The wide usage of a particular type of capacitor will depend on the existence of relevant standards which allows the user to choose equivalent capacitors from different manufacturers.

Currently, no industry standard exists for dry film capacitors for AC applications. However, such a standard is being developed by a committee of the E.I.A. and should be formalized by the end of 1976. This standard will establish minimum performance criteria for any dry film AC capacitors which may be manufactured.

Sales of capacitors to performance specifications implies the acceptance of considerable liability by the capacitor manufacturer. Because of the expense of repairs to lighting fixtures and appliances which have been sold to consumers, the liability due to early failures could easily exceed the cost of the capacitors. A situation of this type occurred during the 1960's when many fluorescent light ballast capacitors failed prematurely. This group of failures occurred when the voltage stress on the PCBs was increased, resulting in a slightly increased rate of degradation by dechlorination caused by corona discharges. The increased failure rate was not apparent on short term tests; the replacement of the failed ballasts was very expensive to the capacitor manufacturer. This problem was solved by the addition of a chemical scavenger to the PCB.

Because of the occurrence of past performance failures and the high potential cost of future failures, the capacitor industry can be expected to be very conservative in the introduction of substitutes for PCBs. Substitutes will be accepted only after the accumulation of substantial long term (3 to 5 years) service testing data. Since the greater biodegradability of the

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substitutes implies that they will exhibit lower chemical stability than PCBs, considerable testing at service conditions will be required to support the general use of any of these materials. This requirement of extensive service testing would be expected to delay the general acceptance of PCB substitutes by 3 to 5 years.

2.7.2 Fire Safety

The use of capacitors is governed by several industry standards which embody the general service experience and risk factors as perceived by industry representatives and fire insurance underwriters. These codes and regulations are specific for various applications of capacitors. The major applications must therefore be considered separately.

2.7.2.1 Utility Use of Power Factor Correction Capacitors

Most of these capacitors are installed in substations or are mounted on poles. In general, the locations of these capacitors are non-hazardous, and there is little risk that fire damage or personal injury will result from the failure of a utility capacitor.

The failure of existing utility capacitors may result in uncontrolled loss of PCBs into the environment. The frequency of capacitor rupture is reportedly quite low (estimated to be .02%/year) and the amount of PCB lost to the environment probably does not exceed 2 to 3 pounds per capacitor rupture. However, because of the large number of capacitors in service and the lack of means for containing any leakage, the total environmental load from this source may total several thousand pounds per year.

Current standards for the disposal of failed capacitors containing more than 2 pounds of PCB requires that they be buried in supervised dry land fills that meet state requirements.(1) In addition, the standards require that these capacitors be labeled with a warning as to their environmental hazards. This label must also contain detailed disposal procedures. The major apparent lack in these standards is in the area of control and disposal of leakage from failed capacitors. The necessity for such control may offset the economic penalties associated with the replacement of PCB capacitors by units which are environmentally less objectionable.

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2.7.2.2 Industrial Use of Power Factor Correction Capacitor

The use of power factor capacitors in industrial plants is governed by state fire regulations and by the National Electrical Code (4) which has been formally incorporated into OSHA requlations.

The National Electrical Code requires that capacitors that contain more than three gallons of flammable liquid be enclosed in a vault or installed in a outdoors fenced enclosure. The definition of flammable liquid is not explicit, but the effect of the Code is to give large PCB capacitors a significant economic advantage compared to those containing other liquids. Proposals are currently being considered to define a class of transformer and capacitor liquids which are self extinguishing. This may eventually lead to a change in the code so that vaults will not be required for large capacitors in industrial applications. This code change is unlikely to be made prior to issuance of the 1981 code.

2.7.2.3 Lighting and Appliance Capacitors

These small capacitors are usually built into the ballast or appliance. Failure of the capacitor prior to the obsolescence of the light or appliance is infrequent, and the capacitor is scrapped as part of the entire assembly. Currently, most of this material ends in municipal landfills. With growing popularity of reclaiming metal values from municipal waste, there will be an increasing amount of PCB which appears as contaminants of scrap steel and is vaporized or burned off in the steel furnace.

The major drawback to the use of substitute materials is the fire safety of the appliance. Completed ballasts or appliances must meet minimum safety standards as specified by tests conducted by Underwriters Laboratories. Because the amount of liquid contained in these capacitors is small, there is probably little increase in fire hazard if a flammable liquid is used, especially if the capacitor is fused to prevent rupture of the case. However, acceptance of flammable liquids in capacitors will have to await action by Underwriters Laboratories, and recent conversations indicate that they have not yet established either specifications or test procedures for electrical equipment containing flammable liquid capacitors.[5]

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3.0 ELECTRICAL TRANSFORMERS

Polychlorinated biphenyls are used as liquid coolants in electrical transformers which are located in enclosed or hazardous locations. PCBs have an advantage over the other major liquid transformer coolant (mineral oil) in that they are nonflammable. Gaseous coolants are also nonflammable, but gas cooled transformers have disadvantages which are considered below. Alternative liquid coolants are probably available, but to date none have been found which have all the advantages of PCBs. The following analysis includes a summary of the purposes of transformers in electrical circuits, heat generation in transformers, currently-used cooling techniques, materials being investigated as substitutes for PCBs, and institutional barriers to the use of substitute materials in place of PCBs.

3.1 Heat Generation in Electrical Circuits

In direct current electrical circuits, the power, P, delivered at a load consisting of pure resistance (e.g., a light bulb) is the product of the electrical current, i, moving through the load and the voltage, V, across the load,

$$P = (V)\ (i) \tag{21}$$

But since current is proportional to voltage for a given resistance,

$$V = (i)\ (R) \tag{22}$$

where R, the resistance, is the constant of proportionality. It follows that power delivered to the load resistance is the product of voltage, V, and the square of the current

$$P = i^2R \tag{23}$$

Since the wires that carry electrical power from the site of generation (be it a battery or an electrical generator) to the load resistance also offer resistance to the flow of electrical current, a portion of the power generated is lost through heating of the wires connecting the load to the electric power source. For a given wire diameter, electrical resistance is proportional to the length of the wire. In many circuits (e.g., an automobile electrical system), the power lost in the transmitting wires is small in

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comparison to the power delivered at the load (such as the headlights). However, in transmitting electrical power over long distances, the resistance of the wires could cause the dissipation of a significant portion of the energy intended for the load.

In alternating current circuits, the power dissipated in a resistance (either in the load or in the wires carrying the power to the load) is also given by $P = i^2R$. (The relation, $P = (V)(i)$, always applies to power dissipated in DC circuits, but in AC circuits the expression only applies when the voltage and current are in phase with each other, which isn't always the case. In most practical instances involving purely resistive loads it is a fairly accurate means by which to calculate the power dissipated.)

The expression, $P = i^2R$, is not influenced by the phase relation between voltage and current and thus applies to both alternating and direct current circuits. It is apparent from this expression that the energy dissipated in a transmission wire having resistance R is proportional to the second power of the current; thus, if the current being delivered to the load were to be doubled, the energy losses in the transmission wire would be quadrupled.

Commercial electrical power is often generated many miles from where it is to be used. There are hundreds of thousands of miles of power transmission lines in this country, and it is not unusual for the electrical power generated in one place to be used hundreds of miles away, which means that a considerable amount of electrical resistance must be overcome in transmitting electrical energy to the user.

The method used to minimize energy losses in transmission lines is to reduce the current, i, and thus minimize the i^2R losses (also known as Joule heating losses) in the transmission wire. In order to deliver maximum power to the load, the transmission voltage, V, must be increased since the power delivered is (as with DC circuits) effectively given by $P = (V)(i)$. Thus, if the transmitted current, i, is reduced by a factor of 2 - which reduces the Joule heating losses of the transmission line by a factor of 4 - the voltage of the transmitted power must be increased by a factor of 2.

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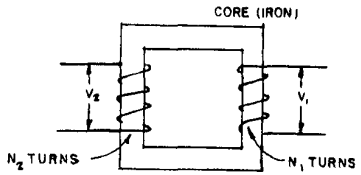
In practice, the electricity which is used in homes at 110 volts is transmitted at voltages ranging up to more than 700,000 volts - roughly 6500 times greater than common wall-socket voltage. As a result, the Joule heating losses are $(6500)^2$, or more than 40 million, times less than if the power were transmitted at 110 volts.

3.2 The Nature and Purpose of Transformers

The purpose of a transformer in an electrical circuit is to transform electrical power from its high-current low-voltage characteristics at the generating facility to the low-current high-voltage characteristics needed for efficient transmission; and then, at or near the site of use, transformers perform the opposite function, bringing the power back into its low-voltage (typically 110v or 220v) high-current form.

A transformer consists of two windings which are joined by a magnetic yoke. An alternating current applied to one winding (the primary winding) creates an alternating magnetic field in the yoke. This magnetic field induces an electric current in the other, or secondary, winding. In a simple transformer, as shown in the following sketch, the ratio of voltages in the primary and secondary windings is equal to the ratio of turns in the windings, or

$$\frac{V_1}{V_2} = \frac{N_1}{N_2}$$



There are two types of transformers used in the electrical power industry: power transformers (used for "stepping up" the voltage at the plant) and distribution transformers (used for "stepping down" the voltage at or near the site of power use). Power and distribution transformers operate on the same principle - they differ only in whether the primary or secondary winding has the greater number of turns. If the transformer is being used for

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stepping up voltage, then the primary side is the one having fewer turns; for stepping down, the primary side is the one having most turns.

The lengths of wire in the windings offer resistance to the flow of electricity, the result being the production of heat in the windings. Heat is also produced by electrical currents induced in the transformer core by same mechanism that induces currents in the secondary windings. Since the electrical resistance of most conducting materials increases with temperature, the efficiency of the transformer (i.e., the ratio of the output power to the input power) is maximized if the transformer is kept at a low operating temperature. Therefore, all transformers used in the electrical industry have provision for cooling, based on either gaseous or liquid coolant.

The coolants in common use today are:

- mineral oil, PCBs — liquid cooled transformers
- air, gas — dry type transformers

3.3 Desired Properties for Transformer Heat Transfer Fluids

The purpose of the heat transfer fluid in a transformer is to absorb the heat produced in the windings and core, to transfer the heat to cooling fins, and to provide electrical insulation within the transformer. The ideal fluid should have the following properties:

Heat transfer: Be a liquid with a low viscosity, high heat capacity, and high boiling point. (The use of low boiling point liquids or gases would require that the transformer be enclosed in a pressure vessel.)

Chemical stability: Not degraded by prolonged exposure to high temperatures. Non-flammable in the event of an electric arc within the transformer and subsequent case rupture. Non-corrosive, with non-corrosive products resulting from exposure to an electrical arc. Low solvency toward other materials used to construct the transformer.

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Electrical properties: High dielectric strength. Low loss-tangent (minimized dielectric heating of the fluid). High resistance to corona formation.

Toxicity: Non-toxic and biodegradable. By-products from exposure to arc should also be non-toxic.

Cost: Low cost.

Availability: Readily available with reliable properties.

3.4 Use of PCBs in Electrical Transformers

PCB cooled transformers account for about 5 percent of all transformers in service.[3,12] The PCB coolant in these transformers is a mixture of 60 to 70 percent PCBs and 40 to 30 percent trichlorobenzene. The PCBs currently used in these mixtures are sold by Monsanto under the trade names of Aroclor 1242 and Aroclor 1254.

The mixtures of PCBs and trichlorobenzene are commonly known by the generic term Askarel. Askarel is defined by the National Electrical Code as "a generic term for a group of non-flammable synthetic chlorinated hydrocarbons used as electrical insulating media. Askarels of various compositional types are used. Under arcing conditions the gases produced, while consisting predominantly of non-combustible hydrogen chloride, can include varying amounts of combustible gases depending on the askarel type". The most commonly used askarel compositions are Inerteen (Westinghouse trade name for 60 percent PCB mixture) and Pyranol (General Electric trade name for 70 percent mixture). The exact composition of both Pyranol and Inerteen have been changed from time to time, but they have almost always been mixtures of PCBs and trichlorobenzene.

Prior to the mid-1950's, the insulating liquid used in many transformers (General Electric formulation) was a 50-50 mixture of Aroclor 1260 (60 percent chlorine) and trichlorobenzene. In the late fifties the benzene component was changed to a mixture of tri- and tetrachlorobenzenes. In September, 1971, at Monsanto's suggestion, the Aroclor component was changed to Aroclor 1254 (54 percent chlorine). The current Westinghouse formulation (Inerteen) utilizes Aroclor 1242.

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The volume of askarel used in various transformers ranges from 40 to 1500 gallons (440 to 16,500 lbs), with an average of about 230 gallons (2500 lbs). One transformer manufacturer, General Electric, estimates the total number of askarel filled transformers put in service in the U.S. since 1932 to be 135,000; virtually all are still in service. Typical lifetime of a transformer is often greater than 30 years, and units that do fail are usually rebuilt and returned to service. The current production rate for askarel filled units is about 5,000 per year, requiring some 10-15 million pounds of PCBs.

Liquid coolants in transformers have better heat transfer and heat capacity characteristics than gaseous coolants. Askarel has the further advantage of being non-flammable. The other advantages of askarels are their high dielectric strength, their outstanding chemical stability, and their relatively low viscosity. Disadvantages , in addition to the environmental threat, are the highly corrosive HCl they produce when arcing takes place and their cost, which is about eight times as much as mineral oil on a volume basis.

Most askarel-filled distribution transformers are located inside public, commercial, or industrial buildings, or on the roof tops of such buildings. No special enclosures or vaults are required except as are necessary to prevent accidental electrical or mechanical contact of persons with the equipment. However, the National Electrical Code does specify vaults for the indoor installation of PCB-filled transformers rated more than 35,000 volts. Askarel-filled transformers are limited by the dielectric strength of the liquid to ratings below 69,000 volts.

Most power transformers are situated in remote locations where fire or explosions are not a threat to property. Mineral oils are commonly used in power transformers in these safe locations. However, some utilities use askarel-filled power transformers at generating stations.

Step up transformers used to supply the high voltage electricity to electrostatic precipitators are usually mounted on or very near the stack. This minimizes the problems associated with the in-plant distribution of high voltage power. These transformers are usually askarel filled units to minimize fire hazard in the usually crowded area of the stack.

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Railroad locomotives which operate on high voltage AC power from overhead catenaries are used in the U.S. Northeast Corridor. Askarel-filled transformers are mounted in the engines or under the self-powered passenger cars, and reduce the catenary voltage to that required by the traction motors. These electric locomotives are mostly limited to passenger service on the Northeast AMTRAK routes and on the commuter lines around Philadelphia and New York. Large askarel-filled transformers are used in the old GG-I locomotives, under the Metroliner cars, in various commuter cars, and in the new E-60 locomotives. (Twenty-six E-60 locomotives are currently being delivered to AMTRAK by General Electric; each locomotive contains 710 gallons of askarel). Penn-Central Railroad operating rules require the use of askarels in all locomotives using the tunnels and stations in New York. This rule has been in force as a fire safety measure ever since an early GG-I locomotive containing a mineral oil-filled transformer was involved in a fire inside a tunnel early in the 1940's.

3.5 Present Alternates to the Use of PCBs in Transformers

Askarel-filled transformers are only used where considerations of fire safety, reliability, availability, and cost make such a unit preferable to an oil-filled transformer or to a dry type transformer. These alternative types of transformers are currently used in 95 percent of all applications, and could, with proper engineering design, be used to replace most of the remaining askarel-filled units. Consideration would have to be given to the specific limitations of these designs that presently make askarel-filled transformers preferable for certain applications.

3.5.1 Mineral Oil-Filled Transformers

If safety were not a consideration, there is no reason why oil-filled transformers could not be used in all applications. Askarel-filled transformers cost about 1.3 times as much as oil filled units of the same capacity, and thus most users prefer the oil-type where possible. The oil-filled transformers are the same size as the askarel units, and are considerably lighter in weight. In addition, mineral oil has somewhat better heat transfer characteristics than does askarel, and an electrical arc in mineral oil results in breakdown products that are non-corrosive.

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The major disadvantage to mineral oil is its flammability. Transformer mineral oil has a flash point of 145°C, and if an arc occurs within the transformer, the breakdown products will be hydrogen and methane which are also flammable. Detailed records of such failures are maintained by the electrical industry.[13] Fire Underwriters do not approve of the use of oils and other flammable liquids for indoor applications; where oil-filled transformers are not specifically prohibited as on-site replacements for askarel-filled units, the National Electrical Code imposes certain restrictions upon their mode of installation.

Oil-filled transformers are used in almost all power transformer applications and for most substation distribution applications where the high voltage from the transmission lines is reduced to 12.8 kv for local distribution. Most rural pole mounted transformers which reduce the voltage to 220 volts are also oil-filled. The issue of flammability only becomes important where the distribution transformer must be buried, as in many urban applications, or located close to, within or on the roof of the building which it serves. Askarel-filled transformers are used for most of these hazardous areas.

Oil-filled transformers can be used in these applications only if they are suitably isolated from flammable structures or if these structures are suitably safeguarded against fires. When transformers are located outside of the building they service, however, the low-voltage power must be brought into the building via cables or insulated buses, incurring additional energy losses due to Joule heating in the additional low voltage transmission lines.

3.5.2 Open Air Cooled Transformers

Transformers can be built without the use of a liquid cooling medium. One type of dry transformer which is quite successful under limited conditions is the open air cooled transformer. In this design, the required cooling is provided by air which passes through the transformer due either to

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thermal convection or forced fan circulation. In those sizes where air cooled transformers are available, they are about equal in price to askarel-filled transformers of the same kva rating. However, the following limitations govern the successful use of open air cooled transformers, and prevent them from being considered for many applications using askarel-filled transformers.

Heat capacity: The power drawn from a transformer usually varies over a fairly wide range. The rating of a transformer is basically governed by the power which it can handle continuously without overheating. If a liquid filled transformer is operated at overload conditions for a short period of time, the liquid will act as a heat sink, absorbing the excess heat produced in the transformer without a rapid increase in temperature. The result of this thermal inertia is that liquid-filled transformers can operate at outputs of up to 200 percent of rated capacity for a period of one to two hours without being damaged.

An air cooled dry type transformer does not have this heat sink available, and is limited to operating at a maximum service rating near its continuous rating. Where the current drawn on the transformer does not vary greatly during the day, this limitation is no problem. However, in most cases the variation in load would require that a dry transformer be sized 20 percent to 30 percent greater in capacity than a liquid-filled transformer for the same application.

Dielectric strength: The liquid coolant in a liquid-filled transformer also provides a significant level of electrical insulation between the various current carrying components within the transformer. Air has a much lower dielectric strength, and open air cooled transformers are limited to a maximum voltage of 25 to 40 kv.

The problem of electrical insulation is even more severe if the open air cooled transformer only operates intermittently. When the transformer is operating, the heat generated within the windings keeps their insulation dry, and maintains a high dielectric strength of this solid insulating material. However, when the transformer is not operating, the coils cool to ambient temperatures and the

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insulation can absorb moisture from the air which reduces its dielectric strength. Therefore, an open air cooled transformer must be carefully dried before being put into service after each time it has been allowed to cool.

One final problem with dry air cooled transformers is due to the tendency of dust to be attracted from the air to the coils by electrostatic attraction. This dust can build up in the coils which blocks the flow of air and causes overheating, or the dust can form conductive paths which short circuit the transformer.

Dry open air cooled transformers are generally limited to dry, clean locations where the load requirements are fairly even and constant, and where the maximum voltage does not exceed 30 kv. This type of transformer is being successfully used in large office buildings, particularly tall buildings where the transformers are located every few floors. Even in this application, there are situations which are beyond the capabilities of the open air cooled transformer; for instance, in the Sears Building in Chicago, which is over 1400 feet tall, the electric power is brought into the building and up to the distribution transformers at 128 kv, which is beyond the voltage limitations of open air cooled transformers.

3.5.3 Closed Gas Filled Transformers

Transformers can be built which use a dry inert gas (usually at an elevated pressure) as a heat transfer medium. These transformers avoid the maintenance problems caused by moisture and dust in open air cooled transformers. However, they are similarly limited in overload capacity because of their reduced thermal inertia compared to liquid filled transformers.

Closed gas filled transformers must be installed in pressure tight containers due to the changes in gas pressure caused by changes in temperature. However, the maximum voltage ratings of these gas filled transformers can be equal to that of liquid-filled units.

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A number of different gases have been successfully used as heat transfer media in closed gas filled transformers. The most common gas used in the U.S. in this application is the fluorocarbon hexafluoroethane (C_2F_6). Nitrogen and sulfur hexafluoride have also been used successfully in certain applications. Helium has not been found to be a satisfactory gas for this application because its low dielectric strength results in corona discharges within the transformer. Hydrogen gas is unsatisfactory as any leak in the transformer would result in a severe fire hazard.

Because of the necessity for the pressure vessel container, gas cooled transformers are 30 to 40 percent heavier than askarel-filled transformers, and cost two-thirds more than askarel transformers (and twice as much as oil-filled transformers). In addition, the gas filled transformers must often be specified in a larger size than the liquid-filled transformers to allow for the expected heavy load peaks of power consumption.

3.6 Current Alternatives to the Use of PCB Cooled Transformers

The National Electrical Code has detailed specifications for transformers which assure that transformer installations meet both fire and shock safety requirements. These safety requirements are achieved by the use of either non-flammable transformers (askarel or dry type) or vaults, or both. The final choice of the type of transformer to be used in each application will be a function of the code requirements and their economic consequences.

3.6.1 Vault Usage Requirements for Transformers

The National Electrical Code 1975[4] considers three types of transformers in connection with indoor vaults: dry type, askarel insulated, and oil insulated.

Askarel insulated transformers installed indoors and rated at more than 35,000 volts must be enclosed in vaults, according to Section 450-23. This same section specified that askarel transformers installed indoors and rated over 25 kva must have pressure-relief vents which must either be vented to the outside of the building, or some other provision must be made for "absorbing any gases generated by arcing inside the case".

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The 35,000-volt criterion also applies to dry type transformers; they must be contained in vaults when in indoor installations. The Code also specifies that dry-type transformers rated at more than 112½ kva must "be installed in a transformer room of fire-resistant construction". Thus, if space is not a consideration, dry-type transformers - which generally occupy a larger volume than equivalent-capacity askarel insulated units - can directly replace askarel-insulated transformers.

In cases where space is not available for the larger-volumed dry-type transformers to replace the askarel-insulated units, or where the dry-type units might emit too much noise for a given location within a building, oil-insulated transformers would be required as replacements for askarel units. Section 450-24 specifies that oil-insulated units must be installed in vaults, but the following exceptions are made:

1. If the total capacity of the transformer does not exceed 112½ kva, vault walls need only be 4 inches thick instead of 6 inches as specified in Section 450-42.

2. Where voltage does not exceed 600, a vault shall not be required if suitable arrangements are made to prevent a transformer oil fire from igniting other materials.

3.6.2 Vault Construction Requirements for Transformers

Section 450-42 of the 1975 National Electrical Code specifies the construction requirements of vault walls, roof, and floor. "The walls and roofs of vaults shall be constructed of materials which have adequate structural strength for the conditions with a minimum fire resistance of 3 hours." (Six-inch thick reinforced concrete is stated in the Code as being typical 3-hour construction.) "The floors of vaults in contact with the earth shall be of concrete not less than 4 inches thick, but when the vault is constructed with a vacant space or other stories below it, the floor shall have adequate structural strength for the load imposed thereon and a minimum fire resistance of 3-hours."

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Vault doors are specified in Section 450-43. "Each doorway leading into a vault from the building interior shall be provided with a tight-fitting door having a minimum fire rating of 3-hours" (as defined by the NFPA). "A door sill or curb of sufficient height to confine within the vault the oil from the largest transformer shall be provided, and in no case shall the height be less than 4 inches." Locks are required for vault doors, and "doors shall be kept locked, access being allowed only to qualified persons". The locks shall be arranged so that vault doors can be easily opened from inside the vault.

With regard to ventilation openings, Section 450-45 specifies the following:

Location: "Ventilation openings shall be located as far away as possible from doors, windows, fire escapes, and combustible materials."

Arrangement: "A vault ventilated by natural circulation of air shall be permitted to have roughly half of the total area of openings required for ventilation in one or more openings near the floor and the remainder in one or more openings in the roof or in the sidewalls near the roof; or all of the area required for ventilation shall be permitted in one or more openings in or near the roof."

Size: "For a vault ventilated by natural circulation of air to an outdoor area, the combined net area of all ventilating openings after deducting the area occupied by screens, gratings, or louvers shall not be less than 3 square inches per kva of transformer capacity in service, and in no case shall the net area be less than one square foot for any capacity under 50 kva."

Covering: "Ventilation openings shall be covered with durable gratings, screens, or louvers, according to the treatment required in order to avoid unsafe conditions."

Dampers: "All ventilation openings to the indoors shall be provided with automatic closing dampers of not less than No. 10 MSG steel that operate in response to a vault fire."

Ducts: "Ventilating ducts shall be constructed of fire-resistant material."

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Section 450-46 specifies the drainage requirements for vaults: "Where practicable, vaults containing more than 100-kva transformer capacity shall be provided with a drain or other means that will carry off any accumulation of oil or water in the vault unless local conditions make this impracticable. The floor shall be pitched to the drain where provided."

Section 450-47 requires that pipes or duct systems "foreign to the electrical installation shall not enter or pass through a transformer vault". Piping or other facilities provided for fire protection or for water cooled transformers shall not be considered foreign to the electrical installation.

3.6.3 Transformer Vault Construction Costs

In an effort to determine the cost factors in the construction of transformer vaults, various construction comp-nies in the Washington, D. C. area were contacted. It was discovered that the incidence of vault construction in existing buildings is virtually zero; apparently all vaults existing in buildings built in the last twenty-five years were constructed as integral parts of the buildings the same as any other room or enclosure in the building. Thus the cost of constructing a vault cannot be easily broken out from the cost of the entire building structure, especially since the prime contractors in the construction industry often subcontract the various facets of the construction work (e.g., concrete forms, concrete pouring, plumbing, ventilation duct work) and the portion of the work required by the vault is included in the cost of construction of the entire building. The construction companies were reluctant to make cost estimates for installing vaults in existing buildings unless detailed drawings were submitted as a basis for estimation, and of the half dozen largest contractors contacted, none had any readily available data from previous such installations, and all claimed such installations were extremely rare.

The National Electrical Code allows the installation of oil-insulated transformers in outdoor locations adjacent to the site of power use. In the Washington area, as in many urban areas, "manholes" are used to house transformers in outdoor locations.

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Useful cost information on manhole installations was obtained through the Potomac Electric Power Company of Washington, D. C. Manholes are precast concrete structures which are commonly installed in public space directly adjacent to the building receiving electric service. (The steel gratings seen in the sidewalks of downtown areas frequently cover manholes containing transformers.)

Manholes are supplied usually by precast concrete product manufacturers. Costs quoted by one manufacturer range from $875 for a 6' x 6' x 6' (inside dimensions) model to $1700 for an 8' x 10' x 7' model. These costs include delivery to the job site and installation into the excavation.

According to Pepco, manholes are usually installed flush against the property line of the building being served. In some cities, the local government pays for the manhole and its installation, but in Pepco's customer service area, the customer pays the cost. (Pepco customers also pay the cost for vault construction when transformers must be installed on private property.) Pepco used to install more than one transformer per manhole, but experience with fires has led them to put only one unit in each hole.

According to Pepco, there are no specific codes relating to manhole construction, but it is likely that local codes influence specific installations. Pepco provides the final 18 or so inches of each manhole installation in order to blend the entire installation into the surface grade; in such cases, and when Pepco has occasion to cast its own manholes, the local building code must be followed.

The average cost of installing a 5½' x 17' manhole is $10,000; no cost-range data were available from Pepco. The labor requirement is typically 600 to 700 man-hours, and total time is about one week. Cost factors include:

1. Working day restrictions - for example, rush hours in some parts of the city restrict work hours to 9:30 to 3:30, but the laborers must be paid for a full days work.

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2. Rain time - the laborers do not work in the rain, but they must be paid.

3. Rocky soil - hand digging (i.e., with pneumatic drills and hammers) may be required in lieu of power shovels. In such cases labor costs - which account for 70 to 75 percent of installed cost - can more than double.

The only other cost for manhole installation is the "public space permit fee", a one-time fee to the local government which is about $20 in the Washington, D. C. area regardless of size of the manhole.

Because they are lighter and easier to handle, dry-type transformers are used very often by Pepco, especially in roof-top applications where noise is not a consideration and ventilation is not a problem. This lightness and ease of handling, in conjunction with the lack of vault requirements for dry-type transformers of less than 35,000 volts, might make roof-mounted dry-type transfomers the most cost effective replacement for askarel-insulated units in areas where the air is relatively free of corrosive gases and dusts which could affect the transformer.

3.7 Substitutes for PCBs in Transformers

Because of the evidence that PCBs are damaging the environment, considerable work is being conducted to find a satisfactory substitute for PCBs in askarel-filled transformers. These efforts by various manufacturers are attracting considerable interest in the business and technical press.[14,15] The goals of these efforts is the development of a heat transfer liquid which will have satisfactory heat transfer properties, be environmentally acceptable, and be non-flammable. These requirements are basically contradictory; the chemical stablilty required for complete non-flammability implies that the liquid may be non-biodegradable and may accumulate in the environment. Therefore, each of the liquids that have been developed sacrifices a certain degree

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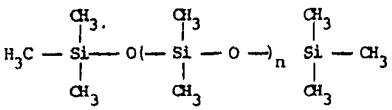
of fire resistance to achieve environmental acceptability. The following liquids have been proposed as substitutes for PCBs in transformers installed in hazardous locations.

3.7.1 Fluorocarbons

Certain fluorocarbon compounds have properties similar to the PCBs, and some study is being carried out in this area.[16] However, fluorocarbons are highly volatile in comparison to PCBs, and they are about six times as expensive at this time - though, of course, higher production volumes would lower their cost.

3.7.2 Silicones

Low viscosity silicone fluids (on the order of 50 centistokes) are also possible replacements for PCBs. Silicones are currently produced by four companies: General Electric, Dow Corning, Union Carbide and Stauffer. The silicone fluid recommended by one producer[17] is polydimethyl siloxane, which has this molecular structure:



Heat Transfer: Silicone fluids have the special advantage of a relatively temperature-independent viscosity. The silicone fluids have somewhat poorer heat transfer characteristics than askarel, but can be substituted directly for askarel in existing transformers, resulting in only a small decrease in the transformer rating.

Electrical Properties:[18]

Dielectric Constant	2.72
Dielectric Strength	400 volt/mil
Resistivity	7.1×10^{14} ohm-cm
Dissipation Factor	1.8×10^{-5} at 100 hz, 23°C

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Flammability: Polydimethyl siloxane has a higher flash point than conventional, non-PCB transformer coolants: 280°C versus 146°C for mineral oil (PCBs have no true flash point). The heat of combustion of 50-centistoke polydimethyl siloxane is lower than that of mineral oil – 7.67 kcal/gm versus 11.0 kcal/gm – and since the siloxones burn more slowly, they are considered poor fuel.[18]

On the Underwriters Laboratories fire-hazard classification (in which water is rated as 0 and ether as 100) polydimethyl siloxane is classified as 4 to 5, which is slightly higher than the 2 to 3 rating given to PCBs, but is considerably less than the mineral oil rating of 10 to 20.[19]

Ecological Persistence: These compounds do not biodegrade, as measured by sewage sludge breakdown to CO_2. However, there is evidence that they partly depolymerize to low molecular weight compounds upon contact with soil and water. Since ultra-violet light decomposes methyl silicones, sunlight exposure may be the mechanism for environmental degradation.

Bioaccumulation: No tendency for bioaccumulation or bio-concentration has occurred in experiments. In the mammals the compound is not adsorbed through the gastrointestinal tract or the skin.

Toxicity: The PCB substitute developed by Dow Corning for transformers is called 02-1090. This is a mixture of polydimethyl siloxanes of various chain lengths which have a viscosity of 50 CS. The literature on environmental and health characteristics of silicones[20] refers to at least six fluids, most of which are probably similar to the OZ-1090 but some of which could be other mixtures with certain additives. By necessity, the usefulness of published toxicological data depends on the validity of the assumption that all of these compounds have identical persistance, bio-accumulation, and toxicity properties.

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A review of toxicological studies of silicones reported the following results:[20]

Dietary Toxicity:

LD_{50} (rats) >28 gm/kg

Extended Feeding Tests:

Guinea pigs - 47 gm/kg/day for extended period - no toxic effect.

Mallard ducklings and bobwhite quail - 5000 ppm for 5 days - no effect.

Rats - 20 gm/kg/day for 28 days - no effect.

Rats - 190 mg/kg/day for 90 days = no effect level.

Beagle dogs - 300 mg/kg/day for 120 days - no effect.

Mice - 3% in diet for 80 weeks - no effect.

Man - FDA allows silicones as food additives at up to 10 ppm.

The major deficiency in our knowledge of the silicones appears to be in their fate in the environment and the toxicity of their breakdown products.

Cost: The silicone transformer fluids currently cost up to twice as much as PCBs on a volume basis.

Availability: Dow Corning is currently completing evaluation of polydimethyl siloxane as a high voltage insulating fluid. They report, though, that a near term 100 percent replacement of PCBs in transformers by this fluid is not possible. If a transformer market were to develop for

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polydimethyl siloxane, the present domestic capacity could only be adequate to supply new transformers. The time lag for a 100 percent replacement of PCBs in transformers by polydimethyl siloxane would be on the order of 5 to 10 years.

3.7.3 High Flash Point Mineral Oils

The flash point of mineral oil is a function of its molecular weight. Crude petroleum can be refined to have any required molecular weight over a wide range. This makes it possible to specify any particular flash point that is desired for the mineral oil transformer liquid. This approach has been taken by RTE Corporation in the development of their proprietary transformer liquid which has the trade name RTEMP.[21]

RTEMP is a highly refined paraffinic mineral oil which has a flash point of 296°C, approximately the same as the 50CS silicone liquid proposed by Dow Corning. To achieve this higher flash point, the oil is refined to have a higher molecular weight and consequently a higher viscosity which reduces its effectiveness in convective cooling. It may be possible to achieve a lower viscosity without sacrificing the fire resistance of the liquid, but this modification has not yet been demonstrated.

The major current advantage of the high flash point mineral oils is their low price relative to silicone and askarel, and their inherent biodegradability and low toxicity.

3.7.4 High Flash Point Synthetic Hydrocarbons

Certain mixtures of synthetic hydrocarbons may result in a liquid having the high flash point characteristics of RTEMP or silicone combined with a relatively low viscosity and satisfactory heat transfer characteristics. The Monsanto Co. is reportedly testing such a mixture

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which has the trade name MCS-1866. No technical details are available on the liquid except that it is claimed to have flammability and heat transfer properties equivalent to silicone at a much lower cost, and to be environmentally acceptable. Monsanto has stated that the technical details will be made public early in 1976.

3.8 Institutional Barriers to the Use of Substitutes for PCBs

The National Electrical Code recognizes only three classes of transformers: askarel, mineral oil, and dry. The Code requirements for askarel and mineral oil transformers differ only in the vault requirements: for transformers located inside buildings or in hazardous locations, vaults are required for all mineral oil transformers, but only for those askarel transformers rated at over 35,000 volts. Askarel transformers are economically attractive for many applications because the savings in vault costs more than offset their higher price relative to mineral oil transformers, and their reliability is better than that of open air cooled transformers. In all cases, technically acceptable alternatives are available to replace askarel transformers; the only limitations are economic.

All of the substitute liquids that have been developed are more flammable than askarels, but less flammable than mineral oil. These liquids do not come within the definition of askarel in the National Electrical Code, and their use is governed by the rules that apply to oil filled transformers. Thus, there is no economic or technological incentive to use these alternate liquids under present Code regulations.

If the Code is to be changed to offer an economic incentive to the use of these liquids, the relative safety of each liquid must be assessed, and a decision must be made as to "how safe is safe enough". In particular, test

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procedures must be developed which allow a realistic estimate to be made of the relative safety of each liquid under conditions which may be expected in service.

Limited testing of the relative fire safety of the various transformer liquids has been conducted by RTE Corporation. The properties of the four liquids that were tested are summarized in Table 3.8-1 which is reporduced from the test results report prepared by Mr. D.A. Duckett of RTE Corporation. (21)

The RTE test consisted of the following procedure for each liquid:

> Four gallons of liquid was heated to 150°C in a closed container. An electrical arc was then initiated below the surface of the liquid. Arc conditions were 4800 amperes at 4800 volts. The resulting explosion and fire was recorded photographically.

The results of this test were as follows: In all four cases, the lid was blown off the container and a fire ball was formed above the container. In the test of the transformer oil, the liquid remaining in the container continued to burn after the fire ball dissipated (as would be expected, as the liquid was heated to its flash point prior to the initiation of the arc). The other three liquids self extinguished within several seconds. Because the fire performance of the RTEMP and the silicone liquids were similar to that of askarel under these test conditions, both RTE Corporation and Dow Corning submitted proposals to the transformer committee of the National Electrical Code to allow the use of "self extinguishing" liquids where present Code regulations require the use of askarel. If these proposals were to be accepted, the use of these liquids would be allowed by the 1978 Code.

There are a number of questions which have not yet been satisfactorily answered concerning the use of the "self extinguishing" liquids. The most important question concerns the realism of the test conditions. It has been suggested that catastrophic arcing is a relatively unusual cause of transformer failure, and that a more frequent cause is prolonged minor arcing which creates

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TABLE 3.8-1

PROPERTIES OF TRANSFORMER LIQUIDS
TESTED BY RTE CORPORATION*

FLUID PROPERTIES:	TRANSFORMER OIL	RTEMP	SILICONE DC-200	ASKAREL
DIELECTRIC				
Dielectric Strength (ASTM D-877) kV (25°C-fluids as received from vendor)	31	37	34	40
Dielectric Constant	2-2.5	2.2	2.74	4.5
Power Factor 50°C	<.01	0.6	0.6	--
100°C	1.0	2.2	0.9	--
150°C	2.5	10.5	1.5	--
Dissipation Factor (ASTM D-150)	.0004	<.05	.0002	.03
Volume Resistivity (ASTM D-1169) Ohm-cm	1.0×10^{12}	1.1×10^{13}	5.6×10^{14}	5.0×10^{12}
THERMAL				
Flash Point °C	150	296	304	--
Fire Point °C	162	321	360	--
Pour Point °C	<-57	-21	-55	-37
Thermal Conductivity 25°C cal/(sec-cm^2-°C)/cm	.000318	.000297	.000360	.000262
Specific Heat (cal/gm/°C) 25°C	.393	.450	.340	.264
Coefficient of Expansion(cc/cc-°C)	.00063	.0008	.00104	.00067
PHYSICAL				
Specific Gravity (ASTM D-1810) 25°C	.883	.883	.961	1.545
Interfacial Tension (dyne/cm)	49.4	25.5	20.8	50.0
Neutralization Number (mgKOH/gram)	<.02	.011	<.01	<.01
Viscosity (centistokes)				
25°C	16	800	50	18
50°C	8	150	30	10
100°C	3	24	16	4
150°C	--	8	12	<3

* Reproduced from report:

"Environmentally Acceptable Insulating Fluids May Replace Askarels", by D.A. Duckett, RTE Corporation; May 8, 1975.

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a flammability problem due to the breakdown products of the transformer oil. If this were the case, neither silicone oil nor high flash point mineral oil would be significantly better than the present transformer oils.

Because of the limited test data that is available, it appears unlikely that the proposals will be approved for inclusion into the 1978 Code. Since the deadline for submission of proposals for this Code revision has passed, the most likely date for any Code revisions is the 1981 Code.

The general acceptance of alternate liquids in place of askarels will only occur after the performance of these liquids has been demonstrated by prolonged service tests under realistic conditions. The effect of the Code is to prevent the testing of alternate liquids in transformers which, under the rules, must be filled with askarels. The inclusion of the Code into the regulations of the Occupation Safety and Health Administration is an additional institutional barrier to the accumulation of adequate performance experience.

3.9 Relative Merits of Alternatives to New Askarel Transformers

The relative merits of the various alternatives that have been proposed are summarized in Table 3.9-1. Special consideration must be given to the suitability of each of the alternatives to the major types of transformers which currently use askarels.

3.9.1 Distribution Transformers

Very few distribution transformers presently use askarels. These transformers are generally installed at the site of major generating plants, and there would be little difficulty in designing these plants so that mineral oil cooled transformers could be used safely.

3.9.2 Power Transformers

Askarel cooled transformers are used in buildings and industrial plants without vaults where the maximum voltage is less than 35,000 volts. Currently available alternates in new construction are:

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TABLE 3.9-1

Relative Merits of Alternatives to the
Use of Askarel Transformers in New Applications

	Toxicity	Fire Risk	Cost/ transformer relative to askarel transformer	Reliability vs PCB	Convertability of present transformers
Mineral oil transformer in vault	excel.	excel.	$5000 to $50,000 more	good	usually no
Mineral oil transformer installed in non-hazardous location	excel.	excel.	$5000 to $50,000 more	good	usually no
Dry transformer	excel.	excel.	1.5x	poor	usually no
Silicone heat* transfer oil	excel.	fair/good	1.3x	good	probably* yes
High flash point* hydrocarbon oil	excel.	fair/good	1x	good	probably* yes

* Use depends on Code regulations being changed to allow self extinguishing liquids as direct equivalents of askarels.

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- Mineral oil transformer installed in a vault
- Open air cooled transformers - limited to clean dry environments with even power requirements. Satisfactory for most office buildings and shopping centers.
- Mineral oil transformers at a site away from the building. This will be satisfactory for most trailer parks and industrial plants except for those locations where space is extremely scarce.

A possible, future, alternative may be to use a "self extinguishing" transformer fluid in those applications where askarels are now required. This alternative requires that major changes be made to the National Electrical Code.

3.9.3 Precipitator Transformers

These are high voltage step-up transformers which are mounted on or near industrial stacks. It should be possible to use mineral oil cooled transformers in all such applications.

3.9.4 Railroad Transformers

These transformers use askarel due to Penn-Central Railroad regulations. However, foreign experience indicates that there is no significant fire risk from the use of more flammable liquids in these transformers: European practice has traditionally been to use mineral oil in locomotive transformers. About ten years ago an experimental transformer was built in France which used an enclosed gas cooled (sulfur hexafluoride coolant) transformer.[22] Although somewhat limited in peak power output (overload conditions) compared to oil-filled transformers, it performed satisfactorily during extensive tests. However, this type of transformer did not gain wide acceptance because it was more expensive than oil-filled transformers, and there was not felt to be any significant safety problem associated with the use of the oil-filled units.

General Motors Corporation recently supplied a demonstration electric freight locomotive to the Penn-Central Railroad for test. This

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locomotive is designated a type GM-6. The transformers in this locomotive were supplied by a Swedish manufacturer, and are filled with mineral oil as Swedish regulations would not allow the use of PCBs even for test purposes. As a result of this material choice, this demonstrator locomotive is not allowed into the tunnels into New York.

Japanese practice over the past four years has been to use silicone oils in new railroad transformers. No service problems have been reported.

AMTRAK is presently negotiating the lease of several new electric locomotives from France. Preliminary specifications call for the transformers to be able to operate satisfactorily with mineral oil, askarel, or silicone oil as the coolant.

3.10 Replacement of Askarels in Existing Transformers

There are currently about 135,000 askarel-filled transformers in service in the United States. These transformers contain an average of 2000 to 2500 pounds of PCBs each, for a total in-service inventory of about 300 million pounds of PCBs. Accidental losses of askarel may occur due to failure of these transformers and accidental spills during servicing. It has been suggested that these losses may be a significant source of PCBs into the environment, and that this source of pollution could be minimized by refilling these transformers with an approved "self extinguishing" transformer liquid.

3.10.1 PCB Losses Due To Transformer Failures

The incidence of failure of askarel-filled transformers has been estimated to be 0.2 percent per year. No more than 1 percent of these failures result in a rupture of the transformer case and spillage of liquid. The usual failure involves only a venting of gases from the transformer safety valve, followed by immediate operation of the circuit breakers to remove the power from the transformer. Thus the expected incidence of spillage is probably on the order of 3 transformers per year containing perhaps 6000 lb of PCB. However, most askarel transformers are installed in buildings or in vaults where there is a provision for containing any leakage. It is probably

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reasonable to assume that the cleanup activities following a transformer rupture are 90 to 99 percent effective in recovering the spilled askarel, which limits the total uncontrolled loss of askarels from transformer ruptures total of 60 to 600 lb per year. If it is assumed that the venting of vapors during a transformer failure results in the loss of an average of two lb of PCB due to evaporation, the total losses from this source will be about 540 lb per year. Thus, the total annual entry of PCB into the environment due to transformer losses is on the order of 4 lb per million lb of PCB in service.

3.10.2 Environmental Effects of An Askarel Replacement Program

The proposal to drain the existing askarel transformers and refill them with an environmentally acceptable heat transfer liquid presupposes the availability of sufficient quantities of a liquid having satisfactory fire resistant properties and heat transfer properties equal to askarel. No such material is currently available. The use of either silicone oil or a high flash point hydrocarbon material would require a change in the National Electrical Code regulations which govern the installation of transformers. In addition, all of these materials have poorer heat transfer characteristics than askarels, which may require the derating of all the transformers.

Assuming that a satisfactory substitute liquid were available, the retrofitting of the existing transformers still faces a number of practical problems. The most difficult problem is the achievement of thorough draining of askarels from the existing transformers. Much of the liquid is held in the insulation of the transformers by capillary action; simple draining of a transformer only removes 80 percent to 90 percent of the liquid. Therefore, it will be necessary to flush each transformer 2 or 3 times with a liquid which will dissolve the remaining askarel, and which is compatible with the liquid used to refill the transformer. This requirement of compatibility could be a major problem; for instance, askarels are immiscible in silicone foils.

It can reasonably be expected that the draining and flushing of each askarel-filled transformer will result in an average of 800 gallons of askarel and PCB contaminated liquid. This liquid must be shipped to an incinerator and burned under controlled conditions. Disposal of the liquid

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could be expected to cost $700 plus the cost of the shipping containers and transportation.

The result of this draining, flushing, and refilling procedure will be a transformer which is filled with 300 gallons of an environmentally acceptable liquid that is contaminated with 10 to 20 lb of PCB. This reduction in the amount of PCBs in service will reduce the severity of potential transformer failures, but will not eliminate the need for careful handling or eventual disposal of the contaminated liquid.

A more serious concern would be the amount of accidental spillage which would occur when the scrap askarel and flushing liquid is shipped to the incinerator for disposal. The current lack of sufficient incineration facilities would require that much of this liquid be stored in drums or tanks for an extended period of time. In addition, the accidental leakage from broken drums and other accidents which can be expected to occur during transportation can be expected to release PCBs and flushing solvent to the environment.

3.10.3 Effect of Leaving Askarel Transformers in Service

The alternative of leaving the askarel in the transformers until they become obsolete or fail is probably to be preferred to retrofitting these transformers with a less toxic liquid. The existing askarel should last the life of the transformers; only infrequently is it necessary to filter the liquid to remove the degradation products of minor internal arcing, and askarel losses during this filter cycle should not exceed 1 percent of the total liquid in the transformer. Askarel for makeup of these losses will not be available once it is no longer used in new transformers; Monsanto has announced its intention of closing the only U.S. PCB manufacturing plant as soon as satisfactory substitutes are available for PCBs in electrical equipment. This should not prove to be a major problem in the maintenance of askarel transformers, as minor losses of liquid can be replaced with pure trichlorobenzene. The resulting mixture will be suitable as long as the concentration of the PCBs is above 50 percent; below this concentration of PCBs, solvent attack on

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the solid insulation may occur. Complete replacement of the transformer required by lack of askarel should be infrequent and should not impose a significant economic burden on the electrical industry.

The decision to leave existing askarel transformers in service also gains time for the solution of the problem of scrapping failed or obsolete transformers. Current specifications require that transformers be drained and flushed before being scrapped. This, however, cannot be expected to remove more than 95 to 98 percent of the PCBs from the transformer internals.

It is currently very unusual for transformers to be scrapped, but when they are scrapped the value of the metal is sufficient to make recycling attractive. There is currently no acceptable facility for the recovery of metal from failed transformers. Special procedures would have to be used to prevent PCB residues from being carried through into the scrap furnaces. This will eventually be a significant problem. Better solutions to the problem can be expected if the problem is delayed by leaving existing transformers in service.

4.0 INVESTMENT CASTING

The investment casting process is a lost-wax casting process in which a pattern is molded from wax and then invested or surrounded by a slurry containing a refractory ceramic. After the ceramic mold is dried to an appropriate strength, the wax pattern is melted or burned out leaving a molded cavity. Molten metal is then poured into the cavity, and solidified by cooling to form a cluster of metal castings. Maintenance of close dimensional tolerances requires that the shrinkage of the wax be carefully controlled during the initial pattern step. This control requires either slow cooling of the pattern while the wax is solidifying or the use of a wax material which shrinks very little upon solidification.

4.1 Function of the Filler Material

One method of modifying the wax to achieve minimal shrinkage is to fill the wax with a finely powdered material that is insoluble in the wax and remains solid at the temperature at which the wax is cast into the molds.

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Because this filler does not change state (from a liquid to a solid) on cooling, it exhibits very low shrinkage, and the resulting slurry of wax and filler will be much more dimensionally stable than will be the pure wax.

The second step in the casting process is to burn the wax residues out of the ceramic mold so that the mold will be completely empty when metal is cast into it. This requires that the filler be volatile at the temperatures used to fire the molds, and that the vapors be non-toxic.

4.2 Use of PCBs in Investment Casting

Some of the pattern waxes, especially those used in the casting of metal parts requiring tight dimensional tolerances, contain decachlorobiphenyl (deka) as the wax filler. Decachlorobiphenyl waxes contain approximately 30 percent (perhaps up to 40 percent) of the decachlorobiphenyl filler.[23] Pattern waxes are recovered and reused several times to form the sprues and gates of the patterns. Wax is apparently used an average of 2.5 times. During the dewaxing process the virgin wax (used to form the pattern) and the old wax (used to form the gates and sprues) are collected as one mixture. Little of the wax is destroyed in the process; therefore, it is probable that the investment casting foundries store or dispose of relatively large amounts of used PCB-containing wax.

It is estimated that approximately one to 1.5 million pounds of decachlorobiphenyl-filled wax is purchased yearly by U.S. investment casters. The cost of the PCB-filled wax is in the range of $0.70 per pound.[24] Imported polychlorinated terphenyls, which exhibit properties very similar to decachlorobiphenyl, is also used as a pattern wax filler. There is only one U.S. producer of deka-filled wax, and this company also produces PCT-filled pattern wax.

4.3 Advantages and Disadvantages of the Use of Deka PCBs in Investment Casting

The deka PCBs have nearly ideal properties for fillers in investment casting waxes. These materials are only slightly soluble in the wax, remain solid at the wax casting temperatures, and volitilize completely at the firing temperatures without charring or burning.

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The only disadvantage to the use of deka PCB is its suspected possible environmental persistence and, by analogy to the other PCBs, its toxicity. No direct evidence of environmental damage from this compound has been found to date.

4.4 Alternatives to the Use of Deka PCBs

Potentially acceptable process alternatives for the deka PCBs could utilize either a replacement filler material or an unfilled wax.

4.4.1 Replacement Filler Materials

Properties required for a filler are: high melting point (over 300°C), high heat transfer coefficient, low thermal coefficient of linear expansion, and minimum ("zero") ash. The following materials have been suggested as possible replacements for deka PCB.

4.4.1.1 Isophthalic Acid

Isophthalic acid has been used as a filler material to a limited extent, but the grade of material that was previously available left an ash residue on firing.[25] A new grade of isophthalic acid, only recently commercialized by AMOCO Chemicals Corp., exhibits much lower ash and metal contents. The various grades of material available from AMOCO are as follows:[26]

Grade	Cost in Bulk	Comments
IPA 85	$0.24/lb	High ash
IPA 99	$0.27/lb	Previous use history
IPA 110	$0.31/lb	Being phased out
IPA 220	$0.35/lb	New - low ash

Although there is a considerable body of literature on phthalic acids and phthalate esters, their environmental fates are not known. Degradation routes properties of degradation products, etc., which are of great importance to an assessment of environmental acceptability have not been studied in depth. It can be surmised that this will be the case for most filler substitutes.

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4.4.1.2 Polystyrene

Polystyrene plastic is available from a number of suppliers including Dow Chemical Co., Monsanto, and Foster-Grant. If this plastic were reduced to a sufficiently fine powder, it would have physical properties equivalent to deka PCB and should perform satisfactorily as a wax filler. The bulk cost of polystyrene pellets is $.40/lb, and the size reduction should cost an additional $.08/lb of filler.

Upon firing, the polystyrene could be expected to depolymerize to styrene which would be volitilized. Styrene vapor has known toxic properties. This potential problem may limit the serious consideration of polystyrene as a wax filler.

4.4.2 Unfilled Waxes

Prior to the use of PCBs or PCT's as fillers, unfilled waxes were used. Industry sources claim that reverting to the use of unfilled waxes would increase production costs by about 10 percent. However, new types of unfilled waxes have recently been introduced to the market, and it is claimed that their properties are equivalent to the filled wax and their cost is slightly lower ($0.60 to $0.65/lb).[27] Although the exact formulation of these waxes is not known, they reportedly contain no chlorinated additives.

4.5 Conclusions - Substitutes for PCB in Investment Casting

Technically adequate substitutes for decachlorobiphenyl filler in pattern waxes appear to be available. Maximum increases in costs would be about 10 percent. The only producer of wax containing PCBs could probably change to other types with very little technical difficulty or economic impact.

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SUMMARY

SUBSTITUTES FOR PCBs

Capacitors

PCBs are used as the dielectric liquid in almost all AC capacitors used by the electrical utilities for power factor correction and in various industrial applications including appliance motors, fluorescent light ballasts, and power supply circuits in television receivers. PCBs are uniquely suited for capacitor applications because of their high dielectric constant, chemical stability, and non-flammability.

A number of different chemicals are being developed as replacements for PCB capacitor fluid. There is not yet sufficient data available on the electrical performance, chronic toxicity, or environmental effects of any of these liquids.

Dry film AC capacitors are also being developed. These capacitors are significantly larger than liquid-filled capacitors and are limited to a maximum of 280 volts. • Satisfactory dry film capacitors will not be available until there are two separate technological breakthroughs: 1) the development of a plastic film that combines a high dielectric constant with a low loss-tangent; 2) the development of winding techniques that exclude all air from the winding of the capacitor.

Although it is probable that satisfactory substitutes for PCBs will be developed within the next 5 years, no such material is presently available and much additional research remains to be done.

Transformers:

PCBs are used as a major component of the non-flammable transformer liquid known as askarel. Only about 5 percent of all transformers are cooled with askarel. These are the transformers which are located in buildings and other hazardous locations where fire resistance is of great importance.

Most transformers are cooled with mineral oil. This liquid is flammable and the National Electrical Code requires that oil-filled transformers be

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installed in fire proof vaults when they are used in buildings. Vaults are not required for askarel-filled transformers that are rated at less than 35,000 volts. Although the askarel-filled transformers are 20 percent to 30 percent more expensive than oil cooled units, the savings on vault construction costs more than offsets the difference.

Other currently available substitutes for askarel-filled transformers are open air cooled transformers, which are limited to lower voltage applications in clean, dry environments, and closed gas cooled transformers which are more expensive than askarel units. Both of these dry transformers have lower overload capacity than do askarel and oil-filled units.

Technically satisfactory alternatives are available to the use of transformers containing PCBs. The present choice of PCB units is based on the relative costs of the alternatives.

Several substitute liquids have been suggested which are less flammable than the currently used mineral oil, but which are more flammable than askarel. These liquids are characterized as being self extinguishing – i.e., they do not continue to burn after being ignited by a momentary electrical arc. Proposals have been submitted to the National Electrical Code to allow the use of these self extinguishing materials under those conditions where askarels are presently specified. Because of the relative lack of service experience with these liquids, it is unlikely that these proposals will be accepted. The next Code revision (1978) will probably continue to recognize only askarel and "oil filled" transformers.

It is likely that the "self extinguishing" liquids will prove to be satisfactory alternatives to PCBs. Substantial experience on the performance of the liquids will be required before the Code requirements will be changed to allow their use. The restrictive Electrical Code, which has been incorporated into the OSHA Regulations, may act to inhibit the accumulation of this data and thereby act to postpone the general acceptance of these substitutes for PCBs.

It has also been suggested that PCBs be drained from existing transformers and replaced with a less toxic material. Analysis of this alternative suggests that it may have a worse effect on the environment than would the continued use of PCB in the transformers.

SUMMARY

INVESTMENT CASTING

Dekachlorobiphenyl is used by one manufacturer in the formulation of investment casting waxes. The deka PCB acts as an inert filler which reduces the shrinkage which occurs when the wax solidifies. Other manufacturers use polychlorinated terphenyls (PCTs) for the same purpose. All of the deka PCB and PCTs used in investment casting waxes are imported.

Several substitutes are available for deka PCB waxes. These include the replacement of the PCB with isophthalic acid, or the use of new low shrinkage non-filled waxes. Complete elimination of deka PCBs from this application should be possible without causing significant problems.

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SECTION IX

PCBs RELEASE AND CUMULATIVE ENVIRONMENTAL LOADS

1.0 ESTIMATES OF FREE PCBs IN THE ENVIRONMENT

1.1 PCBs Losses to the Environment Since 1930, by Use and by Chlorine Content of Molecule

This section includes an analysis of the estimated amounts of PCBs which have escaped to the environment, by molecular chlorine content. The approach and results are summarized below.

Loss factors, which include spillage losses during manufacture or use of the end products and losses due to inadequate disposal methods, are estimated on the following basis:

Use Category	% of Yearly PCB Use Lost to Environment
Closed electrical systems (transformers and capacitors)	5%
Hydraulic and heat exchange fluids	60%
Plasticizers	25%
Miscellaneous industrial applications	90%

Each of the assigned loss percentage factors can be the subject of considerable controversy. Suffice it to say that the choices made appear to be reasonable based on the widely varying information considered.

The following data have been computed on the basis of the production and sales data released by Monsanto on the PCBs. Since by far the largest production has been in the form of Aroclors 1242, 1248, 1254, and 1260, these data are based only on those four mixtures.

"Proportional Use Factors for PCBs" were computed from the Monsanto PCB manufacturing and sales data utilizing the domestic sales by category information. Since the detailed breakdown for the period 1930-1957 was not available, it was assumed that the pattern for this period followed the average

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for the period 1957-1959. Estimates were then prepared of the actual production and use of the individual Aroclors listed above. Table 1.1-1 is a tabulation of the estimated amounts of Aroclors that have escaped into the environment, assuming that 5% of the PCBs used in capacitors and transformers escaped; 60% of that used for hydraulic media, and heat exchange media escaped; 25% of that used for plasticizers escaped; and, finally that 90% of that used in miscellaneous industrial uses has escaped.

These data may be expressed in terms of chlorine content, based on published Monsanto data on the isomers typically present, by chlorine content, in each Aroclor type. The results from such an exercise are presented in Table 1.1-2. The totals in the right-hand column represent the cumulative totals of all escaped PCBs by the year listed at the left.

The computed spectrum of chlorine contents based on the cumulative data on Table 1.1-2 is presented, for selected years, on Table 1.1-3.

The average chlorine content for the set termed "average values" is 4.38 chlorine atoms per molecule, compared to:

Aroclor	Chlorine Content (atoms/molecule)
1242	3.67
1248	4.22
1254	5.35

Thus, the distribution as is comes closest to Aroclor 1248. However, if it is assumed that all mono- and di-chloro biphenyl were biodegraded or otherwise destroyed, then the average chlorine content of the "wild" PCBs would be 4.67, intermediate between 1248 and 1254. If the trichloro isomers were also subtracted out, then the composite average chlorine content would be 5.0, which begins to compare favorably with 1254.

1.2 Total PCBs Accumulation and Current Rates

As a rough estimate of the total PCBs currently available to the biota (in active transport, in biological systems, etc.) in the United States, the total of 172,800,000 lb. from Table 1.1-1 may be reduced by a factor

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TABLE 1.1-1

PCB ENVIRONMENTAL LOAD BY AROCLOR TYPE

[In Thousands of Pounds]

	Aroclor Type					
	1242	1248	1254	1260	1016	Total PCBs
1930-56	18709	5395	5003	3559	-	32466
1957	1991	704	676	932	-	4303
1958	1431	1065	917	783	-	4196
1959	2298	1597	1142	1118	-	6155
1960	2955	1226	989	1191	-	6361
1961	4082	1745	1295	1347	-	8469
1962	3992	1452	1222	1258	-	7924
1963	3648	2062	1166	1503	-	8379
1964	4597	2160	1224	1664	-	9645
1965	5928	2260	1456	1096	-	10740
1966	7010	1932	1247	1041	-	11230
1967	7442	1794	1158	1111	-	11505
1968	7789	1881	1615	954	-	12239
1969	9182	2190	2172	997	-	14541
1970	10072	1536	2575	1044	-	15227
1971	3232	112	717	266	167	4494
1972	48	-	229	20	1045	1342
1973	310	-	399	-	1177	1886
1974	310	-	309	-	1098	1717

Grand Total - 172.8×10^6 lbs.

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TABLE 1.1-2

CUMULATIVE ENVIRONMENTAL PCB LOAD
BY CHLORINE CONTENT

[In Thousands of Pounds]

	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total
1956	561	2540	6210	8221	8936	4017	1759	285	36	32,565
1957	621	2813	6894	9174	10070	4709	2182	360	45	36,868
1958	664	3020	7487	10130	11311	5419	2558	423	53	41,064
1959	733	3351	8417	11584	13086	6388	3085	512	64	47,219
1960	822	3760	9465	13070	14805	7344	3632	607	89	53,580
1961	944	4326	10922	15135	17128	8529	4162	715	89	62,049
1962	1064	4874	12301	17048	19279	9640	4751	816	102	69,973
1963	1173	5389	13693	19095	21575	10835	5437	936	117	78,352
1964	1311	6030	15369	21473	34160	12153	6192	1069	134	87,997
1965	1489	6846	17436	24315	27123	13391	6728	1157	145	98,735
1966	1699	7796	19747	27328	30097	14568	7230	1240	155	109,966
1967	1922	8799	22154	30406	33080	15754	7755	1329	166	121,471
1968	2156	9850	24674	33673	36376	17053	8243	1405	176	133,710
1969	2431	11088	27639	37543	40368	18625	8782	1485	186	148,251
1970	2733	12428	30735	41462	44523	20362	9365	1569	196	163,478
1971	2837	12880	31723	42624	45657	20840	9517	1590	199	167,972
1972	2881	13073	32131	43086	45782	20928	9539	1592	199	169,314
1973	2938	13324	32663	43700	46046	21076	9563	1592	199	171,204
1974	2992	13561	33165	44272	46265	21193	9582	1592	199	172,821

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TABLE 1.1-3

COMPUTED SPECTRUM OF CHLORINE CONTENT FOR WILD PCBs

[In Percent]

	Weight Percentage of Isomers Containing Cl_x								
	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9
1956	1.7	7.8	19.1	25.2	27.4	12.3	5.4	0.9	0.1
1960	1.5	7.0	17.7	24.4	27.6	13.7	6.8	1.1	0.1
1965	1.5	6.9	17.7	24.6	27.5	13.6	6.8	1.2	0.1
1970	1.7	7.6	18.8	25.4	27.2	12.5	5.7	1.0	0.1
1974	1.7	7.8	19.2	25.6	26.8	12.3	5.5	0.9	0.1
Average Values	1.6	7.4	18.5	25.0	27.3	12.9	6.0	1.0	0.1

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accounting for environmental degradation of less chlorinated isomers and other destruction processes. Based on Table 1.1-2, this should be about 20 to 30 million pounds, resulting in a total of free PCBs of about 150 million pounds.

Estimates by Nisbet and Sarofim[1] in 1972 for total PCBs available through air and water dissipation amount to 180,000,000 lb. since 1932. This value is within four percent of the above estimate of about 173million pounds based on the loss factors specified.

Application of the five percent loss factor to the 1974 Monsanto domestic sales yields an estimate of 1,720,000 lb. lost to the environment during 1974, to which should be added a maximum of 50,000 lb. lost from imported materials. The 1974 total of 1,770,000 lb. entering the environment in available forms represents about 1.5 percent of the total amount estimated above to be available to the biota in the U.S.

The 1,770,000 lb. per year amount may be compared with estimates for 1974 by Peakall[2] as follows:

Industrial leaks and disposal	- 880,000 to 1,100,000 lb.
Disposal in dumps and landfills	- 15,000,000 lb.
Total	- 16,000,000 lb.

The figure of about 10 percent loss from the above required to match the 1,770,000 lb. per year loss rate does not appear unreasonable. However, it should be pointed out that the 16,000,000 lb. per year figure for leaks and disposal from Peakall represents almost half of Monsanto's reported 1974 domestic sales, and must be questioned.

1.3 Current PCBs Disposal in Landfills and Dumps

The most important current sources of land-disposed PCBs are:

(1) Solid wastes from the manufacture of PCBs and electrical equipment (including reject capacitors and transformer internals);

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(2) Failed capacitors;

(3) Capacitors in obsolete equipment; and

(4) Municipal solid wastes other than electrical (obsolete equipment, sewage sludge, paper, plastics, etc.)

One relatively minor source is the transformer service industry. This industry handles about 2×10^6 lb. of PCBs annually (roughly half new PCBs). Assuming that 5 percent of the PCBs handled ends up as solid wastes (from filtration, etc.), results in 0.1×10^6 lb./yr. of solid material entering the landfills.

The major sources are treated below. Land-destined solid wastes from production of PCBs, capacitors, and transformers are estimated to contain about 1.2×10^6 lb./yr. of PCBs. Reject capacitors and transformer internals add about 0.7×10^6 lb./yr. to landfills. Since most PCBs used in investment casting are eventually land disposed, this adds 0.4×10^6 lb./yr. Adding in 0.1×10^6 lb./yr. for transport and other losses brings the total of land disposed PCBs from production and first tier use to 2.4×10^6 lb./yr.

The failure rate for PCB-impregnated capacitors is estimated at one percent per year. On this basis, and assuming that the failed equipment enters a landfill or dump, then about one percent of the approximately 450×10^6 lb. of PCBs estimated to be in service in capacitors, or 4.5×10^6 lb./yr., can be expected to be landfilled.

Capacitors which have not failed but are contained in obsolete equipment (TV sets, light fixtures, etc.) also end up in land disposal sites. This applies to small capacitors only, and it is estimated that one percent of the total are discarded in this manner each year. The amount of PCBs involved is $(0.01 \times 270 \times 10^6)$, or 2.7×10^6 lb./yr.

The amount of PCBs currently contained in land-disposed municipal and industrial wastes other than that assignable to transformers and capacitors

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is difficult to estimate. Approximately 160 million pounds of PCBs have been used in plasticizer and other "open end" applications or in "semi-closed" applications such as hydraulic or heat transfer systems. Most of this usage occurred between 1960 and 1972, and it is likely that up to 80 percent of the total is either free in the environment or already in land disposal sites. The rest of this material, estimated to be on the order of 30 million pounds can be thought of as being literally "in service" or used and awaiting disposal. A prime example of the latter is used carbonless copy paper currently residing in files and awaiting disposal or recycling. It is estimated that about seven percent of this 30 million pound reservoir, or 2.1 million pounds, enters land disposal sites each year.

In addition, it is estimated that 0.3 million pounds of free PCBs in the environment are added to land disposal sites each year from a variety of sources (sewage sludge, dirt, garbage, etc.). This brings the total for municipal and non-electrical wastes to 2.4×10^6 lb./yr.

Source	PCBs Added to Landfills and Dumps, lb./yr.
Wastes from Production and First Tier Use	2.4×10^6
Failed or Obsolete Capacitors	4.5×10^6
Capacitors in Obsolete Electrical Equipment	2.7×10^6
Other Municipal and Industrial Wastes	2.4×10^6
Wastes from Transformer Service Industry	0.1×10^6
Total	12.1×10^6

Peakall's[2] estimate of 16×10^6 lb. of PCBs for leaks and disposal in 1974 is about 30 percent higher than the above total. Peakall[2] also estimated a total of 50×10^6 lb. for leaks and disposal during 1970, which is over two-thirds of Monsanto's 1970 reported domestic sales of about 73×10^6 lb. In the absence of no other comparable data, we estimate a current land disposal rate of between 10×10^6 and 15×10^6 lb./yr.

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It should be noted that several large first-tier users of PCBs are not currently land-filling their solid wastes, but are storing the drummed wastes on-site in anticipation of potential regulations on disposal of such wastes. The wastes being stored are estimated to contain at least 0.5×10^6 lb. per year of PCBs; this is included in the above analysis as being finally disposed of in landfills.

1.4 Release of PCBs via Industrial Effluents (Waterborne)

Based on data obtained from industry, the following average PCBs waste loads for water effluents were estimated:

PCBs Production	1117 lb./yr.
Capacitors	2139 lb./yr.
Transformers	62 lb./yr.
Total	3318 lb./yr.

This number is very small in comparison to the estimated 10×10^6 to 15×10^6 lb. per year of PCBs going to landfills.

The above values for industrial discharges do not include PCBs discharged to municipal systems for those plants having discharges to rivers (ten plants). In the production category, all discharge is to a municipal system.

It should be noted that the above waste loads represent current industrial practice. It may be assumed that, prior to knowledge of the adverse environmental effects of PCBs, much of the types of material currently landfilled was not disposed of properly and thus entered the environment directly.

1.5 Spills of PCBs During Transport

The most complete set of transportation spill data for PCBs available to us are for the period 6/74 to 6/75. The spills during transport and the quantities involved are as follows:

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Location	Gallons Spilled
Trion, Ga.	117
Lawrence, Ala.	600
Erie, Pa.	120
Unknown	~100*
Total	937 (10,213 lb.)

In addition, during this period, three railroad capacitors failed in the New York City area, spilling on the order of 50 lb. each, or a total of 150 lb. Since this occurred during transit, we chose to add this amount to the above total, for a grand total of 10,363 lb. spilled in the transportation-related incidents. This probably represents a minimum figure, since transport of defective product units (capacitors and transformers) and of PCBs containing wastes can be expected to release PCBs.

On the basis of the above, a tentative number of 10,000 lb. per year of transportation-related spills of PCBs is advanced.

*Capacitor shipment via truck overturned; leading units and soaked dirt removed from site for subsequent incineration.

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(2) Peakall, D.B., "PCBs and Their Environmental Effects", CRC Review, 5, Issue 4, 1975.

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SECTION X

INADVERTENT AMBIENT REACTIONS AS ROUTES OF ENTRY OF PCBs INTO THE ENVIRONMENT

1.0 INTRODUCTION

This is a report of a preliminary investigation into the ways that PCBs could enter the environment even if they were no longer manufactured, imported, used or disposed of in the U. S. The work focused on the reactions of aromatic compounds, particularly the biphenyls, and how the conditions found in ambient surroundings in the environment could lead to the inadvertent and undesirable synthesis of PCBs. Specifically the major question addressed was whether chlorination water treatments could convert biphenyl contamination into PCBs.

Beyond that, there are questions of the likelihood of the breakdown of compounds such as DDT, followed by recombination to produce a PCB; the breakdown and rearrangement of dyestuffs to form PCBs; and other potential routes to the inadvertent synthesis of PCBs.

When a candidate route is identified, one needs then to determine the probability of that reaction proceeding, and the reaction rate. Also, the determination of what relevant pollution loads and concentrations occur in wastewater or clean water systems is an obviously important factor. For this study, the objective was primarily the identification of PCB formation routes which could be significant. Studies to determine kinetics of these reactions have not, to our knowledge, been performed.

2.0 COMMERCIAL BACKGROUND, PRODUCTION AND PROPERTIES OF BIPHENYL

2.1 Origins and Commercial Usage Background

Biphenyl (previously known as diphenyl and phenyl-benzene) was first reported in 1862 by Fittig. In 1867 Berthelot identified it as the main product generated when benzene vapors were passed through a hot tube. During 1925-1926, Dr. Herbert H. Dow carried out experiments with diphenyloxide, using it as a heat transfer fluid in a steam power process. In 1927, Theodore Swann of the

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Federal Phosphorus Co. was asked to supply biphenyl in commercial quantities for use as a heat transfer fluid in the refining of lube oils. He set up a pilot plant for this purpose.

Soon after, the Swann Corp. developed the "Aroclor" series of PCBs. Early in the 1930's, Monsanto took over this production. About that time Dow also entered into the field, developing "Dowtherm A", a eutectic of 73.5% diphenyloxide and 26.5% biphenyl. Dowtherm has been a popular heat transfer fluid since that time.

During the 1950's, the advantages of using biphenyl as a mild fungicide in individual fruit wrappers were appreciated. Later, biphenyl was used as a kraft paper and boxboard impregnant and as a coating in closed fruit packages. In the 1960's, the usage as a carrier for dispersed dyes began. All of these biphenyl applications have continued to be important up to the present. Hydroxybiphenyls are also used as preservatives, and aminobiphenyls are used as dye intermediates.

2.2 Production Methods and Rates for Biphenyl

The two principal producers in the U. S., Dow and Monsanto, both synthesize biphenyl by the thermal dehydrogenation of benzene.

At temperatures of 700-850°C, benzene reacts by a homogeneous gas-phase reaction (in which a benzene molecule joins with another benzene molecule or with a polyphenyl molecule, liberating hydrogen and forming diphenyl or higher polyphenyls), or by a heterogeneous gas-solid reaction giving carbon and hydrogen. Most process development work has been directed to repressing the second reaction, which is known to be catalyzed by metals, particularly nickel, iron, and copper.

In 1964 biphenyl appeared on the U. S. market as a by-product of phenol produced by the partial oxidation of benzene. Benzene can be oxidized to phenol and biphenyl with hydrogen peroxide as the oxidant. Other more recent sources of biphenyl are as a by-product of the hydrodealkylation production of naphthalene, and as a by-product of the dealkylation of toluene to benzene. The latter stream,

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one of the bottoms from the benzene plant, has a fuel value of 1 to 2¢/pound. However, a 97 mol % pure biphenyl can sell for about 6¢ per pound. By-product streams of this type are rich in biphenyl (typically 15-20% by weight). It can be seen that wastewaters from a process like this could be the source of methyl biphenyls found in water supplies.

Coal tar amounts to about 3% by weight of coal processed. Biphenyl is part of the heavy oil fraction, along with substituted naphthalenes, accounting for about 10% of the tar. Thus biphenyl generation could amount to one pound for every ton of coal processed for liquid fuels. As more emphasis is placed on coal conversion, the potential contribution to the environmental load of biphenyl may increase.

One degradation route to biphenyl was found. It is possibly of importance since it indicates a pathway from chlorinated terphenyls to PCBs. When vapors of terphenyls are mixed with hydrogen and heated to 650-850°C., benzene and biphenyl are formed. Best results are obtained when 4 to 6 mols of hydrogen per mol of terphenyl are used (based on a Monsanto Patent). Typical terphenyls are Dow's "Therophen" and Monsanto's "Santowax".

The above indicates that PCBs could be produced by the incomplete incineration of chlorinated terphenyls, or possibly from terphenyls themselves in the presence of decomposing PVC or other source of chlorine.

There is no recorded production data for biphenyl for any period of time. Data for biphenyl is included in the "other non-fuel" uses of benzene, which includes BHC, anthraquinone, and several other compounds, in addition to biphenyl. This whole category has amounted to between 50 and 100 million gallons of benzene equivalent per year over the last 30 years.

One industry source estimate for the early 1970's was 5 million gallons of benzene equivalent going to biphenyl. Allowing for the recent burgeoning interest in dye carriers by doubling that value, there could be as much as 80 million pounds of biphenyl sold annually in the U.S. This does not seem too unreasonable since one localized area of Georgia accounts for 22 million pounds per year.

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On balance, a "best estimate" of 50 million pounds per year current biphenyl use would seem appropriate.

2.3 Properties and Characteristics of Biphenyl

Biphenyl is a rather stable organic compound, and it is resistant to thermal and radiation degradation. Some of its properties are given in Table 2.3-1.

TABLE 2.3-1 PHYSICAL CONSTANTS OF BIPHENYL

Solubility in water at 20°C., mg/l	7.5
Melting point, °C	69.2
Freezing or congealing point of commercial product, °C	68.5-69.4
Boiling point at 700 mm, °C	255.2± 0.2
Flash point, °C	113
Fire point, °C	123
Ignition temperature of dust cloud, °C	650

	Temperature, °C			
	100	200	300	350
Vapor pressure, atm		0.251	2.436	5.509
Liquid density, g/cm^3	0.970	0.889	0.801	0.751
Heat capacity, cal/g	0.427	0.509	0.590	0.631
Heat of vaporization, cal/g	95	82	68	60

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3.0 PROVEN BIPHENYL REACTIONS YIELDING PCBs

The two categories of biphenyl reactions examined in this section are the direct chlorination of biphenyl and the joining of two chlorinated phenyl groups into the biphenyl configuration.

3.1 Chlorination of Biphenyl

Although conflicting statements can be found in the literature, it is accepted that biphenyl is more easily chlorinated than benzene due to less resonance stability in the biphenyl. The behavior of biphenyl is complicated by the non-coplanarity of the two rings. Because of repulsion between the 2 and 2' hydrogen atoms, the rings of biphenyl itself have an angle of about 45° between their planes. This non-coplanarity greatly diminishes the resonance interaction between the rings, and is believed to make biphenyl more prone to reaction than benzene.

Since benzene can be brominated with bromine at 0°C in the presence of iron, and also chlorinated with chlorine in the presence of iron at 50°C, we can expect significant reaction of biphenyl with chlorine in the presence of iron below 50°C. Also, solid biphenyl reacts with bromine vapor to give first 4-bromobiphenyl, and then 4, 4'-dibromobiphenyl. Biphenyl melts at about 70°C. The commercial production of PCBs by chlorination of biphenyl in the presence of an iron catalyst is conducted above 70°C in order to obtain and maintain the molten state for ease of transport and for better mixing with the added chlorine. The higher temperature conditions may also be important in the formation of the higher chlorinated homologs, but this is also dependent on contact time. The chlorination is exothermic.

The ease with which biphenyl may be chlorinated to two isomeric monochlorobiphenyls is best illustrated by an early description of a pilot plant synthesis by Jenkins, McCullough and Booth, of the Federal Phosphorus Company, in 1929.[1] They used a temperature just high enough to melt the biphenyl, and achieved iron catalysis by using iron filings. Schmidt and Schultz and Kramers had shown that antimony pentachloride was a catalyst for the reaction.[2, 3]

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The method used by Jenkins and coworkers led to the formation of 2-chlorobiphenyl and 4-chlorobiphenyl. In this reaction some dichlorobiphenyl is always produced, with the amount depending on the temperature of chlorination and on the quantity of chlorine added. Higher temperatures during the chlorination produce higher percentages of dichlorobiphenyl. When the theoretical amount of chlorine for monochlorobiphenyl is added, considerable dichlorobiphenyl is formed.

The general conclusion derived from this synthesis evaluation is that it is quite reasonable to expect that chlorine contact with biphenyl at ambient temperatures will yield PCBs at a measurable rate. The effects of temperature, dilution by air or water, lack of iron catalyst, presence of other catalytic compounds, presence of UV radiation, and other reaction conditions present in the environment are not known.

3.2 Reactions Combining Phenyls to Produce Biphenyls

Two aromatic nuclei can be joined to form a biphenyl by interaction of a diazonium salt and a hydrocarbon (benzene) under the catalytic influence of metallic copper or zinc (Gatterman procedure). In the method developed by Ullmann, many biphenyl derivatives are made by the treatment of aryl halides with copper powder. The halogen atom must be reactive. NO_2 is an example of an activating group. These two procedures are of special interest because reactants similar to the above reactants, or their progenitors, have been found in public water supplies. Examples are mono-, di-, and trichlorobenzene and chlorinated nitrobenzene.

Hutzinger, Safe and Zitko synthesized twenty-three chlorobiphenyls using a number of different routes.[4] The compounds ranged from mono- to decachlorobiphenyl. The general procedure used involved the use of diazo compounds. The specific chloraniline, selected to give the desired PCB, is heated in concentrated hydrochloric acid to about 50°C, then cooled to -5°C and diazotized with a solution of sodium nitrite in water. The mixture is stored for 30 minutes at this low temperature, then filtered. The filtrate is added to cold, vigorously stirred benzene, and a solution of sodium acetate (or

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sodium hydroxide) in water. The mixture is stirred for 12 hours at 25°C., and then the PCB is recovered from the benzene layer. As an example, by this method, starting with 2, 3, 4, 5 - tetrachloroaniline, they synthesized 2, 3, 4, 5 tetrachlorobiphenyl.

They also prepared decachlorobiphenyl by the exhaustive chlorination of Aroclor 1268. The Aroclor was mixed with twice its weight of antimony pentachloride, and heated for four hours at 150°C.

Wolf and Kharasch showed that irradiation of orthoiodophenol in benzene gave 2-hydroxybiphenyl with a 65% yield.[5]

The conclusion drawn from this review of the reactions of a number of aryls is that there are a number of low temperature reactions (0-50°C.) that are capable of yielding biphenyls. In addition, some of the reactants have already been identified as present in water supplies.

4.0 BIPHENYL USAGE IN HEAT TRANSFER FLUIDS, DYES AND PACKAGING

Although the prime usage for biphenyl is the production of PCBs, it also has important use in heat transfer fluids, as a dye carrier, and as a paper or paperboard impregnant.

4.1 Heat Transfer Fluids

In heat transfer fluids, for the temperature range 250-360°C, biphenyl is used alone, or in combination with other compounds. Dowtherm "A", or Diphyl in Europe, is the combination of biphenyl with diphenyloxide. A mixture of bi- and terphenyls was used as a coolant-moderator in the AEC prototype organic-liquid cooled nuclear reactor at Piqua, Ohio.

4.2 Dye Carriers for Polyesters and Polyolefins

Disperse dyes (dye and carrier combinations) are the most widely used dye type for unmodified polyesters. Dye uptake is rather slow, and frequently pressure-dyeing above 100°C is used. Also, carriers or accelerants like biphenyl are used to cause the fiber to swell and allow more rapid penetration of the dye into the fiber.

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Polyolefin fibers are also difficult to dye. Their non-polar nature and impermeability are the problem properties. However, dye carriers such as biphenyl penetrate these fibers and leave the insoluble dye residue within the fiber. Of course, most of the carrier would be expected to leave the fabric in dye-setting and washing processes. Disperse-dyed polypropylene fibers generally lack the bright colors sought in apparel, but they are used in tufted carpets and upholstery fabrics.

4.3 Biphenyl as a Mold Preventative in Packaging

Biphenyl itself has been used for many years as a mild fungicide in citrus fruit wrappers and packaging. The 2-hydroxybiphenyl sodium salt has also been used as a preservative, germicide and fungicide.

The use of biphenyl as one ingredient in impregnated tissue for wrapping citrus fruit began in the Middle East, then grew in the U.S. An odor control agent was added since biphenyl has such a pronounced odor.

Practically all of the biphenyl containing coating is now applied to the inside of the corrugated cardboard cartons used for shipping citrus fruit; or the biphenyl is applied to a pad of sheets placed inside the carton.

It would be impossible to ship citrus fruit across the U.S. in cartons, without a blue mold preventative like biphenyl. Years ago, "orange crates" of open lattice wood were used to let air circulate through and reduce mold formation. However, this exposed the fruit to the drying effects of air, external molds, water, dirt, etc. The new sealed cartons prevent all these problems, but absolutely require a mold retardant. The coating on cardboard or in tissue consists of a petroleum jelly or similar base with about 15-20% of biphenyl.

During the mid-1950's, the FDA investigated the toxicity of biphenyl, and some of the results of this investigation emerged as a threat to the future of the $40 million/yr. segment of the kraft paper industry devoted to making the cardboard cartons, liners, wrappers etc. for citrus fruit shipping. The Institute of Paper Chemistry (IPC) was chosen to determine methods of analysis,

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and to referee an investigation of the potential problem. As a result of the work by IPC, biphenyl was given a clean "bill-of-health" by the FDA and has continued in use.

4.4 General Biphenyl Occurrence in the Environment

The above descriptions of biphenyl usage indicate a potential for its widespread occurrence. Of particular interest here is the occurrence of biphenyl in industrial usages where water treatment by chlorination is practiced, as in paper recycling and dyeing operations.

5.0 PCBs GENERATION AND WASTEWATER EXPERIMENTS IN A MAJOR U.S. BIPHENYL USAGE LOCALITY

For the past three years, Dr. Peter Gaffney of the Biology Department of Georgia State University has been investigating the problems of biphenyl and PCBs contamination of a watershed in northwest Georgia. He has also conducted experiments on the conversion of biphenyl to PCBs. Support was provided by the Georgia Environmental Protection Division. He estimates that this locality uses about 22 million pounds per year of biphenyl as a dye carrier in carpet dyeing. This relatively small geographical area accommodates 250 to 300 mills representing 65% of the world's carpet and rug industry.

Also, W. C. Tincher of the Environmental Resources Center of Georgia Institute of Technology has been studying the problem of biphenyl effluents from polyester carpet manufacturing in Georgia. Other workers have been concerned with the residual odor of biphenyl in carpets.

In New England, R. A. Hites of MIT has been analyzing river water for biphenyl wastes from dyeing processes.

Dr. Gaffney originally became interested in the problems of biphenyl and PCBs in water when he was called to investigate a BOD problem at a municipal waste treatment plant. Two-thirds of the flow to that plant (4 million gpd out of a total of 6 million gpd) came from a carpet dyeing mill. When looking for agents that might affect the biomass in the activated sludge portion of the plant, two questions arose:

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1. Could the biphenyl (used as a dye carrier) discharged from the mill be affecting the biota, since biphenyl is a known mold suppressant?

2. Could the biphenyl be converted to PCBs during waste treatment chlorination, and could the PCBs exert a harmful affect on the biota, as well as contribute toxic organics to downstream water supplies?

Although these studies are still underway, preliminary data indicate that PCBs can be formed in the suspected manner.

The original report of Gaffney's work told of finding 18 ppm of PCBs in the scrapings from the surfaces of trickling filter rocks in the municipal treatment plant.[6] At the time, no PCBs were detected in the influent.

This seemed a strong indication of PCBs formation within a municipal treatment plant. The plant was using about 350 pounds per day of chlorine for influent odor control and effluent disinfection.

When it was later discovered that there was an upstream transformer plant using PCBs, further testing indicated there were detectable PCBs in the intake water to the mill and the town.

Dr. Gaffney continued his previous work on chlorination of organics as they pass through municipal treatment plants.[7] The tests and data are considered preliminary at this time, and further reaction and analytical data are highly desirable.

In laboratory tests, detectable levels of PCBs were formed when 10 mg/l of biphenyl were added to deionized water, held at 20°C, and then 1 mg/l of chlorine was added and the reactants kept in contact for one hour. Fifteen peaks were formed in the electron capture chromatogram (a hexane in water control gave four peaks with the same treatment). When iron was included in the reaction mix, four more peaks were formed (total of 19). It is believed that these peaks are largely chlorobiphenyls. Addition of an Aroclor to the pure water resulted in the growth, by 50 fold, of the peak height for dichlorobiphenyl due to chlorination.

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When municipal wastewater was analyzed before and after laboratory chlorination, as described above, the dichlorobiphenyl peaks increased in height by ten-fold.

Although the tentative conclusion from this work was that PCBs can be formed through chlorination of biphenyl in wastewater under laboratory conditions, extrapolation of the results to actual wastewaters from industrial sources is probably premature. Even more tenuous, but of equal interest, is the possibility of further chlorination of PCB molecules via chlorination.

However, it should be noted again that the use of biphenyl as a dye carrier leads less to its dissipation in products than to its eventual destruction or discharge as waste. Assuming that half of the biphenyl so used appears as waste, a biphenyl to PCB conversion of even 0.01 percent during chlorination treatment for the 22 million pounds per year of biphenyl in northeast Georgia corresponds to the generation of over 1,000 lb/year of chlorinated biphenyls in that area.

6.0 POTENTIAL DEGRADATION AND SUBSEQUENT REACTION OF DDT AND RELATED COMPOUNDS IN THE ENVIRONMENT TO FORM PCBs

It appears possible that there are a number of compounds in the environment that could be partially decomposed and then reacted with their own decomposition products, or with other reactants, to produce PCBs.

As early as 1969, Plimmer and Klingebiel reported that DDMU, dichlorobenzophenone, and dichlorobiphenyl, were all products of the photolysis of DDT or DDE in methanol at 260 nm ultraviolet radiation.[8] This conversion may be sensitive to reaction conditions. In the same year, Mosier, Guenzi and Miller did not observe formation of PCBs or DDMU when they subjected solid DDT or DDT in hexane to UV irradiation at 254 nm.[9]

Since that time, most researchers publishing on this topic have suggested the possibility of conversion of DDT to PCBs. Peakall and Lincer stated that the possibility that PCBs could be derived from DDT should be considered.[10] They did not believe this could occur in metabolic processes in tissues. However, they felt that UV catalyzed free radical reactions to form dichlorobiphenyl from DDT could be expected in the atmosphere.

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Although they could envision tautomeric shifts leading to various isomers of dichlorobiphenyl, they could not theorize a route to more highly chlorinated biphenyls by these DDT reactions. They also pointed out that PCBs extracted from biological materials matched well with the PCBs found in Aroclors like 1254 (one-half pentachlorobiphenyl, and about one-quarter each of the tetrachloro and hexachloro homologs). Thus, if DDT degradation to dichlorobiphenyl were taking place, further chlorination would also have to take place, by some other reaction, to lead to the material found in biological specimens. Peakall and Lincer also point out that the ethane component between the two rings in DDT is the weakest part of the structure and is the site at which most transformations of DDT take place. The PCBs, not having that weak point between the two benzene rings, thus are expected to be more stable than DDT, which is the case. Maugh again reported on the DDT conversion potential, apparently unaware of the Plimmer and Klingebiel report, and showed the potential for vapor phase photolysis.[11]

Peakall, in his recent comprehensive review, "PCBs and Their Environmental Effects", does not cite other references for other mechanisms of DDT conversions.[12] However, Kothny, in a letter to the editor of Chemical and Engineering News, states a case for the formation of gaseous chlorine from particulate chlorides under the influences of ozone and solar radiation.[13] He states that the chloride loss from particulates, formed by the evaporation of water from sea spray, "has been known for some time". Kothny then goes on to attribute PCBs formation to the reaction between a wide range of aromatics that could be present in the atmosphere, and chlorine, formed as described above. He also suggests potential PCBs formation from all manner of waterborne aromatics by action of municipal and industrial chlorination of pure and wastewater.

7.0 COMPARISON OF POTENTIAL INADVERTENT AMBIENT REACTIONS

Of the types of reactions cited in this section as holding potential for inadvertent ambient production of PCBs, the possible chlorination of biphenyl during industrial and muncipal water and waste treatment appears to the authors to have the most significance. In general, the other reactions cited would

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require two steps (chlorination plus condensation of aryls or decomposition of DDT followed by recombination of selected fragments); they also would be expected to involve compounds present in relatively low concentrations compared with potential biphenyl concentrations in some industrial waste streams.

For all of these reactions, however, mono- and dichlorobiphenyls would be the expected products. Although these are believed by many researchers to be significant (especially in an aquatic environment), it is generally accepted that they are more easily biodegraded and less bioaccumulative in comparison to the more highly chlorinated PCB homologs. The possible formation of more highly chlorinated PCBs from mono- and dichlorobiphenyls is thus also of interest to the environmental PCBs problem.

8.0 PCBs FOUND IN THE EFFLUENTS OF THE MACHINERY AND MECHANICAL PRODUCTS MANUFACTURING INDUSTRY

For some time it has been suspected that PCBs could be found in the effluents of other industrial categories which are not recognized as being sources of PCBs entry into the environment. A review of data presented in the draft Development Document For Effluent Limitations Guidelines for the Machinery and Mechanical Products Manufacturing Point Source Category (EPA Contract No. 68-01-2914, Volume 3, June, 1975) indicates high concentrations of PCBs, in the order of 2 to 28 mg/l, in the effluent of the plants grouped in this category.

This group of industries encompasses 173 different product group segments manufacturing over 4000 different products in over 100,000 separate plants. These products include such varied goods as wire, tractors, x-ray equipment, sporting goods, automobiles, television picture tubes, and jewelry.

Because of the variations in manufacturing operations from plant to plant, categorization of this industry was based on the manufacturing processes utilized, whereby a specific plant was defined by the applicable process subcategories which describe its overall operation. Rationale used in subcategorizing this group of industries was that the manufacturing processes, not the product, generate the effluent discharge.

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Based on the above, this group of industries was divided into the following twelve general manufacturing subcategories:

Subcategory 1	Casting and Molding - Metals
Subcategory 2	Mechanical Material Removal
Subcategory 3	Material Forming - All Materials Except Plastics
Subcategory 4	Physical Property Modification
Subcategory 5	Assembly Operations
Subcategory 6	Chemical-Electrochemical Operations
Subcategory 7	Material Coating
Subcategory 9	Molding and Forming - Plastics
Subcategory 10	Film Sensitizing
Subcategory 11	Dockside Ship Building Activities
Subcategory 12	Lead Acid Battery Manufacture

The PCBs concentrations in the raw waste from the overall machinery and mechanical products manufacturing point source subcategories, as abstracted from the abovementioned draft Effluent Guidelines Document, are presented in Table 8-1. This table shows the minimum, maximum and mean PCBs concentrations as found from sampling and analysis work conducted by the contractor on 240 raw waste streams in the point source category. As reported in this document, all samples were taken downstream of the manufacturing processes, but prior to any treatment.

It can be seen from Table 8-1 that PCBs concentrations in the effluent from this group of industries are much higher than those reported for the major PCBs user industries (capacitor and transformer industries). Within the machinery and manufacturing industries PCBs could be used in paints, inks and plastics, as wax fillers in casting operations, as hydraulic and heat transfer fluids, and in lubricants.

It should be mentioned, however, that there are questions as to the validity of the analytical techniques used during this study. Subsequent studies conducted by Versar Inc. on Subcategory 12 (lead acid battery manufacture) under EPA Contract 68-01-3273 have indicated no detectable levels of PCBs in the

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TABLE 8-1

PCBs Concentration in the Effluents of the Machinery & Mechanical Products Manufacturing

Subcategory No.	Manufacturing Operations	PCBs Concentration mg/l (1)		
		Min.	Max.	Avg.
1	Casting & Molding of Nonferrous Metals	0.2	5.1	2.1
2	Mechanical Material Removal	0.2	63.3	6.997
3	Material Forming - All Materials Except Plastics	0.2	63.3	9.867
4	Physical Property Modification	0.2	100.0	12.842
5	Assembly Operations	0.2	104.4	15.553
6	Chemical-Electrochemical Operations	0.5	2.8	1.65
7	Material Coating	0.2	224.8	18.241
8	Smelting and Refining of Non-ferrous Metals	0.2	18.0	9.1
9	Molding and Forming - Plastics	-	None	-
10	Film Sensitizing	0.3	123.9	28.136
11	Dockside Ship Building Activities (2)	-	None	-
12	Lead Acid Battery Manufacture	7.5	30.0	18.75

Note: (1) Information obtained from the Development Document for Effluent Limitations Guidelines for the Machinery & Mechanical Products Manufacturing EPA Contract No. 68-01-2914, Vol. 3, June 1975.

(2) No water effluent; all solid wastes.

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effluents; however, evidence of the presence of chlorinated hydrocarbons was found. Effluent Guidelines study on Subcategory 10, Film Sensitizing Industry, is currently underway. According to the information presented in Table 8-1, this subcategory was demonstrated as having the highest levels of PCBs concentration in the outfalls. Verification sampling work to be conducted on these effluents will provide a further test of the validity of the data in Table 8-1.

It is considered quite likely that effluents from industries other than those directly involved with the production and process usage of PCBs may exhibit significant amounts of PCB contamination. Much of this contamination, if found, could be attributed to past usage of PCBs and products containing PCBs, although, as stated elsewhere in this report, current usage must also be considered a possibility. To our knowledge, no significant effort to determine the extent of PCBs contamination from such sources has been made.

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SECTION XI

MOVEMENT OF PCBs IN THE ENVIRONMENT — GENERAL DISTRIBUTION MODEL

1.0 INTRODUCTION

Thus far in this report, the history and current status of PCBs production and usage, treatment and disposal aspects, and gross estimates of current environmental distribution have been presented and discussed. Transport of PCBs within the environment is extremely important in the assessment of future environmental distribution of PCBs. In turn, knowledge of future PCBs distribution will allow the assessment of potential regulation of PCBs production and usage. Projection of future biological effects also depends upon the distribution of the substance of interest.

Transport of PCBs between soil, water, sediments, the biota, and the atmosphere is of obvious local environmental importance. Measurable amounts of PCBs have been found in Antarctic ice, showing that atmospheric transport over long distances does occur. Transport phenomena at the various phase interfaces are of obvious importance to the mobility of any environmental contaminant, but in most cases, and this is particularly true of PCBs, such transport properties are not known and have not been treated successfully in a theoretical manner. On the other hand, analysis of the transport and distribution of a given contaminant requires sufficient knowledge of basic transport processes on which to base reasonable estimates; the estimates can then be evaluated using an internally consistent model and available experimental data.

A simple, first-order mass balance model has been constructed to treat the overall PCBs economy of an artificially bounded region of the lithosphere. In order to test the validity of the model, it was applied to Lake Michigan and the associated drainage basin. Lake Michigan was selected for this application because of the existence of a considerable body of

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recent data on PCBs concentrations, because of the environmental and commercial significance of PCBs contamination in Lake Michigan, and because this lake, in spite of its size, represents a relatively closed system (estimated water retention time of 90 years).

The total environmental load of PCBs, and its variation with time, represents a very important input to the mass balance model. An analysis of available data was performed to provide this input, one important result of which was an estimate of the variation of atmospheric fallout rate with time.

Atmospheric fallout appears to be the most important source of PCBs entering Lake Michigan, although this may not be the case for other areas (the lower Hudson River is one possible exception). For example, in 1974, atmospheric fallout onto the lake and its drainage basin accounted for approximately 85 percent of the PCBs input to the lake.

The rationale for the model is described in Section 2.0 below. Subsequent sections describe the application to Lake Michigan and the results and conclusions therefrom. The development of the model is presented, in full, in Appendix D to this report, and the supporting data used are tabulated in Appendix E.

2.0 RATIONALE FOR MODEL DEVELOPMENT

The first order model derives basically from the assertion that the total of PCBs entering a bounded region of the lithosphere must be fully accounted for by: (1) Incorporation into specific phases of the bounded region; (2) Loss from the region via mass transport; and (3) Degradation by processes operating within the region.

In application, the region under study is selected to be sufficiently large and well defined that adequate averaging can be accomplished. The Lake Michigan area, which meets the above criterion, was selected as a suitable region for study. The region included the nominal drainage basin of the lake

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in order to provide an estimate of the PCBs entering the lake from runoff.

After suitable boundaries were defined, an overall mass balance was constructed. The source function was constructed so as to account for all point and non-point sources. The distribution over the various internal phases of the system (aqueous solution, biota, and sediment) was then estimated. Additional terms were introduced to account for PCBs loss from the region due to mass outflow and surface evaporation. There was apparently no need to introduce a term to account for degradation since such processes are thought to be of small importance for PCBs. The form of the mass balance was then as follows:

$$B(t)\ \Delta t = \Delta M_W + \Delta M_B + \Delta M_s + \Delta M_O + \Delta M_E \qquad (2\text{-}1)$$

where:

- $B(t)$ is the source or driving function which describes the input rate for PCBs;
- ΔM_W is the change in the mass of PCBs dissolved in the aqueous phase of the region;
- ΔM_B is the change in the mass of PCBs contained within the biota of the region;
- ΔM_s is the change in the mass of PCBs contained within the sediment of the region;
- ΔM_O is the mass of PCBs carried out of the region by (water) mass transport; and
- ΔM_E is the mass of PCBs carried out of the region by evaporation (codistillation).

2.1 Time Dependence of the PCB Input Rate [B(t)]

The distribution of PCBs between phases within the region is governed by processes which are assumed to act independently of the actual concentrations involved. The time dependence of equation 2-1 is therefore contained in the driving function, [B(t)].

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Sensitive analytical methods for PCBs have been available only for a few years; consequently a sufficiently reliable and detailed data base to allow the direct determination of B(t) is not available. In view of this, it was necessary to construct a model which could be fitted to a direct estimate of B(t) for a specific time, in order to approximate the appropriate time dependence of B(t). The details of the computation by which B(t) was determined are contained in Appendix D (Section 2). For the purposes of this summary, it is sufficient to state that the major input of PCBs to the region selected (Lake Michigan) was from atmospheric fallout; thus the time dependence of B(t) was estimated from knowledge of the time dependence of the fallout.

Table 2.1-1 is a summary of the input PCB from all sources during the period 1973-1974 and is a summary of the detailed data which are presented, along with suitable citations to the sources of these data, in Appendix E of this report.

Table 2.1-1

Summary of PCB Input Sources (1973-1974) to Lake Michigan

Point Sources	1.6×10^3 lbs/yr
Lake fallout	6.4×10^3 lbs/yr
Basin fallout*	5.4×10^3 lbs/yr

Then $B(t) = B(1973\text{-}1974) = 13.4 \times 10^3$ lbs/yr

* It is assumed that 50 percent of the basin fallout actually enters the lake as input(1)

3.0 APPLICATION OF THE MODEL TO LAKE MICHIGAN

The results of an analysis of PCBs distribution within Lake Michigan are summarized in Table 3.0-1 (The details of the computation are given in Section 3 of Appendix D).

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Table 3.0-1

Overall PCBs Balance for Lake Michigan Area
During the Period 1930-1975

Total Input	1.49×10^5 lbs.
Total in Solution (Water)	1×10^5 lbs.
Total in Biota	3.64×10^3 lbs.
Total in Sediment	1.7×10^4 lbs.
Total in Outflow	9.07×10^3 lbs.
Total Evaporated	1.93×10^4 lbs.

The last entry in Table 3.0-1 indicates that some 13 percent of the total input to the lake has been lost by evaporation (codistillation) from the surface.

The concentration of PCBs in the aqueous phase and the (average) concentration in the biota were calculated; the results are displayed in Table 3.0-2.

Table 3.0-2

Derived PCB Concentrations in Lake Michigan
Water and Biota Over the Period 1930-1975

Date	C_{water} (ppt)	C_{biota}* (ppt)
1930	0	0
1935	4.9×10^{-4}	1.97
1940	1.34×10^{-2}	5.36×10^2
1945	7.12×10^{-2}	2.84×10^3
1950	0.28	1.12×10^4
1955	0.68	2.72×10^4
1960	1.60	6.4×10^4
1965	2.92	1.17×10^5
1970	5.35	2.14×10^5
1975	9.10	3.64×10^5

*The average biotic concentration is taken as $4 \times 10^4 \bar{C}_{water}$.

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The values presented in Table 3.0-2 are lake-wide averages so that considerable variations from these values are to be expected from point to point within the lake; for instance between the northern portions and the heavily contaminated regions on the southwestern shore. In addition, because of the considerable spread in species-specific concentration factors (and the wide variation in intra-species concentration factors) it can be surmised that PCB concentrations in higher predators could easily have exceeded the ppm level by 1960.

4.0 RESULTS AND CONCLUSIONS

4.1 Results

Even though the model used is only first order, it is apparently able to describe the relative significance of the natural processes which control the distribution of PCBs. The strong focus on fallout as the primary input source of PCB to Lake Michigan suggests the need for further study of the nature of the processes by which PCBs become airborne and thus become part of the available atmospheric reservoir.

The attempt to model the atmospheric reservoir of PCBs, discussed in Appendix D (Section 2), yields results that indicate significantly greater cumulative atmospheric loads than the preliminary estimate, made by Nisbet and Sarofim,[2] of a cumulative atmospheric reservoir of 3×10^4 tons up to 1970. The estimate of Nisbet and Sarofim leads to a half-life, from the model, for PCBs in the atmospheric reservoir on the order of eight years. This value is considerably in excess of the reported lifetime measurements, on the order of 20 to 40 days, for atmospheric PCBs.[3] However, the observation that significant levels of PCBs are found in present snowfalls and in packed snow in the Antarctic[4] suggest that the applicable half-life may indeed be considerably longer than 20 to 40 days.

It is suggested that further refinement of the environmental distribution model presented in Appendix D (Section 2) will lead to a resolution of

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this apparent discrepancy. This refinement will focus attention on the nature of the physical processes involved in atmospheric transport of PCBs and may suggest methods of reducing PCB fallout in the future.

The observation that evaporation and/or codistillation seems to be a significant process by which PCBs are returned to the atmosphere is of importance. It should be noted that the magnitude of the evaporation rate constant necessary to achieve mass balance in Lake Michigan is in excellent agreement with that computed from the simple kinetic theory of gases and also with that computed from the theory of codistillation discussed by Mackay and Wolkoff[5] (see Section 4 of Appendix D for a detailed treatment of this subject).

The observation that the PCB input to Lake Michigan from point sources seems to be a rather small part of the total input suggests that reduction of point source PCB effluents may only slowly correct the present problem.

4.2 Conclusions

The first order mass balance model described herein seems useful in describing the historical situation as it explicitly addresses the question, "How did we get here?" The model requires refinement before it can be used to allow a reasonable estimate of future conditions. Significantly more detailed data are required as to the temporal variation of inputs and concentrations as well as on the internal transport processes by which localized concentrations are smoothed and distributed over the whole body. While the present model seems to deal very well with the situation that obtains during an interval of rising aqueous concentrations, there seems to be little experimental or theoretical guidance as to what will happen if, in the future, aqueous concentrations begin to fall. It is not known whether the biota and the sediments will act as reservoirs to return their PCB loads to the system. The processes, if any exist, which will eventually remove or inactivate the PCBs already in the lithosphere are not known.

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The application of this model to the situation in Lake Michigan seems successful. It will be of interest to apply it to regions which are more complex or of larger scale.

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SECTION XII

REGULATORY ACTIONS ON PCBs

1.0 INTRODUCTION

The risk of increased accumulation of PCBs in the environment as well as appreciation of the difficulties involved in imposing workable environmental controls in most end-use manufacturing operations have led some manufacturers and a number of government agencies to take steps to regulate PCBs or to restrict some uses of PCBs where emission risks are obviously quite uncontrollable.

1.1 Measures Taken by the Manufacturers

In 1971, Monsanto Company, the major producer of PCBs, instituted a program which led to voluntary restriction on sales by the Monsanto of PCBs for all uses except the manufacture of sealed electrical equipment (transformer and capacitor applications). Sales for heat transfer applications were phased out in 1972 while sales for other non-electric applications were discontinued in 1971. As a result, current production related to point source discharges of PCBs are more controllable than in years prior to 1971 when PCBs were widely used in thousands of "Open-End" and "nominally closed" operations.

Furthermore, by 1971, at Monsanto's suggestion, the capacitor and transformer industries formed a standards committee. The members of the committee include representatives from the three affected industries, EPA, Department of the Army, Department of Agriculture, the Tennessee Valley Authority, the National Bureau of Standards, and the General Services Administration. Also represented were the Certified Ballasts Manufacturers Association, the Electronic Industries Association, the Institute of Electrical and Electronic Engineers, and the National Electrical Manufacturers Association. In the fall of 1972, under the auspices of the American National Standards, this committee published PCB handling and disposal guidelines (ANSI-C107-1-1974). This document establishes procedures for labelling, shipping, general handling and proper disposal of liquid and solid materials containing PCBs. This standard

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has been proposed also by NEMA and is currently being used voluntarily by the transformer and capacitor industries.

The above measures taken by the manufacturers could be effective in PCB control if they were supported, implemented and enforced by the Federal Government.

1.2 Measures Taken by the U.S. Government

The Government of the United States has taken a number of steps with the objective to reduce the PCBs content in foodstuffs and reduce emissions from all sources. The following Federal laws are relevant for the regulation of PCBs.

1.2.1 Food, Drug and Cosmetic Act (21 U.S.C. 301 et seq.)

The Food and Drug Administration has set tolerances for PCBs contamination of animal feeds, foods, and food packaging in its final rule-making document published on July 6, 1973 (Federal Register, Vol. 38, No. 129). These tolerances, expressed as parts per million are as follows:

(1)	Milk (fat basis)	2.5
(2)	Dairy products (fat basis)	2.5
(3)	Poultry (fat basis)	5.0
(4)	Eggs	0.5
(5)	Complete and finished animal feeds for food producing animals	0.2
(6)	Animal feed components	2.0
(7)	Fish and shellfish (edible portion)	5.0
(8)	Infant and Junior food	0.2
(9)	Paper food - packaging material	10.0

The Food and Drug Administration provides, upon request, the analytical methods used for enforcing these tolerances.

The FDA enforces the FDC Act by various means, including inspections of food establishments to determine whether the provisions of the Act are being violated. These inspections include the collection and analysis of food samples. Some of the samples are taken by FDA on a routine surveillance

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basis to determine the presence of specific contaminants. However, the actual number of FDA conducted routine sample and analyses is few and this agency relies heavily on information on the known or suspected existence of specific instances of food contamination.

1.2.2 The Egg, Meat and Poultry Acts

The Consumer and Marketing Service of the U.S. Department of Agriculture (USDA) administers three acts relevant to the PCB problem: the Egg Products Inspection Act (P.L. 91-597); the Wholesome Poultry Products Act (P.L. 90-492); and Wholesome Meat Act (P.L. 90-201).

These authorities apply to meat, egg or poultry products from the time they reach the processing plant until they are purchased by the consumer. Once they leave the plant, they are also under the FDC Act.

The Department of Agriculture uses FDA guidelines for its Egg, Meat and Poultry Acts.

1.2.3 The Clean Air Act (42 U.S.C. 1857 et seg.)

Mr. David Young of the Southern California Coastal Water Research Project in a report prepared as part of an ORD (Environmental Research Center - Corvallis) contract acknowledges that the air contributes about one-third of the total PCB loading of the ocean. His conclusion that air is a significant route of PCB transport is based on effluent and aerial fallout measurements made in the coastal areas of Southern California.

The current understanding is that air transport of PCBs is a contributor to the PCB loading of other media. However, the conclusion reached by the pollutant strategies board of the Strategies and Air Standard Division is that the air act of 1970 is not an effective legislative measure for control of PCBs; but that monitoring for PCBs should be considered for control. The recommendation made at that time was to control PCBs by regulating the production, use and disposal of PCB-containing products.

The general authorities contained in the clean air act are not applicable to the majority of PCB discharges since PCBs from most PCB applications,

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such as for closed electric systems, are not emitted into the air by the operation of industrial and municipal facilities. In these applications, PCB emissions are associated with accidental losses and waste disposal in landfills. Additionally, PCBs enter the air via the burning of refuse containing PCB waste products. These types of air emissions can be controlled only by preventing PCB products from being incorporated into the refuse. Control of emissions from landfills may require specifications on how waste is covered and, in some cases, the application of plastic materials to prevent sublimation. However, in the case of PCB applications for the investment casting category, PCBs can enter directly into the environment from the operation of furnaces which are used for purposes of setting the mold and removing the wax from the mold. In this latter application, the air act can be used as an important tool for the regulation of PCB entry into the environment.

1.2.4 Federal Water Pollution Control Act (33 U.S.C. 466 et seq.)

Section 304(a) of FWPCA

Section 304(a) of the Federal Water Pollution Control Act (FWPCA) authorizes the Administrator of EPA to enforce state water quality standards established by the States and approved by the Federal Government, if the State is not adequately enforcing the standards.

In 1973, water quality criteria were proposed to limit PCBs to 2 ppt in ambient waters. The 1973 proposed level has been more recently reduced to 1 ppt due to evergrowing concern on the health and ecological effect of PCBs and on the basis of further review of available data.

Section 307 (a) FWPCA

A national effluent standard for PCBs has been proposed under Section 307(a) of FWPCA.

Section 311 of FWPCA

In 1974, the Office of Air and Water Programs acted to minimize accidental spills of PCB through the enforcement of Hazardous Substances Section of the Water Pollution Control Act. Currently, pursuant to Section 311 of this

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act, proposed guidelines on the levels of harmful quantities of PCBs accidentally released into navigable waters and rates of penalties for such spills are being developed.

Section 304(d) of FWPCA

Section 304(d) of the effluent guidelines promulgated for several industrial categories contain limitations on PCBs. For example, effluent guidelines promulgated for the steam electric power generating category contain limitations of "No Discharge" for PCBs. Furthermore, EPA reports that NPDES permits limiting PCB discharges have already been issued for several facilities.

1.2.5 The Refuse Act of 1899 (33 U.S. C.407)

Section 13 of the 1899 Refuse Act forbids the discharge of any wastes, other than municipal wastes, into navigable waters without a permit. This act would be an effective tool in the control of PCB discharges into the waterways if the permit program required the reporting of PCBs as a separate item. Presently this is not a requirement.

1.2.6 The Occupational Safety and Health Act (29 U.S.C. 651-678)

Chemical hazards in the workplace are regulated under the Occupational Safety and Health Act (OSHA). The Secretary of Labor, in cooperation with the Secretary of Health, Education and Welfare, is authorized to set and enforce occupational safety and health standards applicable to businesses affecting interstate commerce.

In Title 29, Section 1910.93, the limits set for chlorodiphenyl compounds as an air contaminant are 1 mg per cubic meter for Aroclor 1242 and 0.5 mg per cubic meter for Aroclor 1254, based on 8 hours average exposure. The Department of Labor could enforce these limits on PCBs.

1.2.7 Act to Regulate Transportation of Explosives and other Dangerous Articles (18 U.S.C. 831-835)

The Department of Transportation (DOT) regulates the transport of hazardous substances under the Act to regulate transportation of explosives

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and other dangerous articles. Under CFR Title 49, Subpart G amended February 27, 1973, DOT classifies poisonous substances into three categories:

Class A - highly poisonous material
Class B - moderately poisonous material
Class C - irritating material

The responsibility for insuring that this standard is met remains with the manufacturer and the shipper.

1.2.8 Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 135-135K)

On October 29, 1970, the Pesticides Regulation Division, administered then by the Department of Agriculture, issued a notice (PR Notice 70-25) to all pesticide manufacturers and distributors to eliminate the use of polychlorinated biphenyls and polychlorinated terphenyls from their formulation and products. Presently, there should be no pesticides on the market or in use containing PCBs.

Under the FIFRA act, all pesticides shipped in interstate commerce must be registered with the EPA. Presently, EPA can refuse to register a product if it will cause injury to humans or the environment if used as directed. A product already registered with EPA can be cancelled if it is found that it no longer meets the criteria of registration.

Congress is currently considering bills to renew the FIFRA act. More than 20 amendments to FIFRA are pending in the House and Senate. One of these amendments, if adopted, will give the Secretary of Agriculture the power of veto over EPA by requiring USDA concurrence in procedures leading to pesticide cancellation or changes in classification or regulation. This amendment will loosen EPA's controls on dangerous pesticides.

1.2.9 Needs for Federal Control

It can be summarized that currently four government agencies, the Monsanto Company and NEMA comprise the regulatory forces restricting the use and distribution of PCBs. EPA, OSHA, FDA and USDA have authorities to regulate

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and monitor food levels, disposal into waterways and housekeeping and safety practices in the work place. EPA forbids the use of PCBs in pesticides and regulates their discharges into the waterway. OSHA can regulate PCB hazards in the work place. FDA forbids PCB use in food processing machinery and limits PCB levels in food, feeds and paper food-packaging material. USDA follows FDA guidelines in egg, meat and poultry products. Monsanto manufactures more degradable PCBs and sells them only for selective uses, and NEMA recommends standards and guidelines for handling and disposal of PCB containing materials. Each of these available authorities has a limited focus and is inadequate to prevent more PCBs from entering the environment.

Both Monsanto's and NEMA's actions are voluntary and have no law behind them for enforcement. The government has no power to control and restrict imports of PCBs and if it desires to restrict the use of PCBs in selected applications, it has no authority to impose this restriction on any manufacturer.

The above actions can only be implemented through the proposed Toxic Substances Control Act (TSCA). TSCA would give EPA the needed authority for formal banning of certain PCB uses and sanctioning National Standards and Guidelines for handling and disposal of PCB containing products. Thus EPA could deal with the PCB problems in a far more orderly and effective manner. Additionally, the TSCA would enable EPA to require testing for health and ecological effects of new chemicals which are being proposed as substitutes for PCBs. Thus, this measure could prevent new chemicals from creating health and ecological problems similar to those from PCBs. This preventive approach of controlling chemicals is a more reasonable and cost effective method than the current approach of corrective measures after the damage has been done. Therefore, the passage of the Toxic Substances Act by Congress is an important step in dealing with problems such as PCBs.

1.3 International Decisions and Agreement

There are currently no regulations to restrict the importation of PCBs as a chemical for use in applications banned by the Monsanto Company. As a

result, PCB is being imported by a few companies for use in several "open-end" or "nominally-closed" applications.

In 1972, with hopes to bring about a multi-national understanding on PCB uses, the United States asked the Organization for Economic Cooperation and Development (OECD) through its Environment Committee to review national policies on PCBs and also identify products moving in international trade which contained PCBs. In October, 1972, OECD, whose members include all major western industrialized countries plus Japan and Australia, met to discuss the U.S. proposal to control manufacturing and trade of PCBs.

In the October meeting the OECD Council decided that for adequate protection of health and environment, PCBs should be controlled by the actions of individual member countries. It was agreed that in order to insure that home production was not substituted by imports, control action by governments through licensing or other means was essential. It was further recognized that means to insure proper collection of used materials, safety in transport of raw PCBs and assessment of substitutes for PCBs were of utmost importance.

Details on the council's decisions were issued on February 14, 1973. The major thrust of the decision was:

A. PCBs should be used for industrial or commercial purposes in the following applications:

- As dielectric fluids in transformers and capacitors
- In heat transfer applications (other than that for applications in foods, drugs, feeds and veterinary products)
- As hydraulic fluid in mining equipment

With respect to the above uses, the OECD Council recommended that PCBs should only be used if adequate environmental controls were exercised and when the requirement for non-inflammability outweighed the needs.

B. Manufacture, use, recovery, disposal, import and export of PCBs should be controlled and regulated. Special labelling for bulk PCBs and PCB-containing products should be instituted

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and safety specifications on containers and transport should be established.

C. Manufacture, import, and export of PCB-containing products should be controlled and efforts should be directed to eliminate the use of PCBs in "open end", "nominally-closed", and small capacitor applications.

D. Amount of material manufactured, exported, imported, incinerated and consumed by PCB type should be reported and any substitute used for PCB should be identified, characterized and defined.

The decision of OECD leaves it to the member countries to go beyond the council's agreements and it further encourages the governments to phase out PCB uses wherever possible. OECD council's decision or even more stringent measures are currently being exercised in all member countries.

1.4 Measures Taken by Foreign Governments

The measures taken by foreign governments are, in some instances, quite severe; especially in Japan, where a large scale poisoning episode, resulting in the disease syndrome "YUSHO", occurred in 1968 (after a heat transfer fluid leaked in a rice-oil pasteurization plant). In other countries, like the Netherlands, the control measures are quite informal. The main thrusts for PCB control are found in two main areas; those taken by the manufacturers and those required by the legislative process.

1.4.1 Measures Taken by Manufacturers - Limitations of Sales

Several nations have voluntarily limited sales of PCBs. The spectrum of limitation ranges from restrictions to specific fields of manufacture that are considered to be non-polluting or controllable to total suspension in the manufacturing process.

Since 1972, Japan has banned production and importation of PCBs; the United Kingdom has restricted sales of PCBs to all applications with the exception of their usage as a dielectric fluid, while Germany has lessened

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this restrictive measure to include the heat-transfer and hydraulic-fluids industries.

1.4.2 Measures Taken by Some Governments

1.4.2.1 PCB Producing Countries

Actions taken by governments differ widely, ranging from acceptance of the measures taken by the manufacturers to a more strict regulation.

France

The government has taken no active legislative action and has accepted the local manufacturers decisions. These include:

- Complete cessation of sales for heat transfer purposes, in pharmaceutical and food industries, paper production of carbonless copying paper, marine paints and cutting oils.
- Providing information to manufacturers about the dangers of PCB, with a view to cancelling their use in or on products in contact with foodstuffs.

Germany

The government is taking the approach of supporting the manufacturers' decision to stop selling PCB and is pursuing the voluntary signing of bilateral agreements to restrict the amount of imports. Additionally, tolerances of PCB in foodstuffs are being established.

Japan

PCBs have been under governmental control since 1972. There have been practically no production, import or export of PCBs in this country since 1972. The two companies, Kanegafuchi Chemical and Mitsubishi-Monsanto, which had been producing PCBs in Japan ceased their operation and suspended their sales in 1972. One exception has been the production of PCBs for railroad transformers which was discontinued in September, 1973. The use of

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existing stocks in railroad transformers is permitted, subject to the conditions that there be no discharge to the environment. Beginning in 1976, paper plants will be prohibited from accepting PCB contaminated paper for recycling purposes and they will be required to build treatment facilities to meet the general discharge standards.

Imports of equipment using PCBs have been decreased drastically since 1972. For these products importers must cooperate with the users to ensure that the components containing PCBs are properly disposed.

Manufacturing of PCBs are rigidly controlled by the Ministry of International Trade and Industry (MITI). Any company who desires to manufacture PCBs must apply to MITI for a permit. The Japanese government anticipates a total ban on PCBs in 6 to 10 years.

These efforts have had remarkable results, and the environmental levels of PCB in Japan have subsided and are expected to continue diminishing.

United Kingdom

The government is taking no official action and is accepting the decisions of the manufacturers. Additionally, there is a high duty on imported PCBs (about 23%).

1.4.2.2 Non-Producing Countries

Canada

Initial activities are under way to collect necessary data for restricting PCBs pursuant to a new Environmental Contaminants Act which should be enacted by 1976.

Finland

The use of carbonless copying paper is totally banned and legislation is being proposed to require prior authorization for the use of PCBs by the Ministry of Social Affairs and Health. Furthermore, compulsory labelling and disposal instructions are being introduced.

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Netherlands

A gentleman's agreement is in effect that PCBs will no longer be used in the manufacture of paints, inks, lacquers, adhesives, resins, wire and cable coatings, lubricating oils, hydraulic fluids and copying paper.

Norway

Since October 1971, only the Ministry of Social Affairs can authorize the use of PCBs.

Sweden

Since June 1, 1972, only the environmental protection board can authorize the use of PCBs or compounds containing PCBs. Furthermore, compulsory labelling and identification of PCB content on the wrappings have been introduced.

Switzerland

Since October 1972, PCBs or products containing PCBs may not be sold to the public or to light industry. Heavy industrial use is subject to prior authorization.

1.5 U.S. Customs Regulations

Pursuant to Customs Bureau Directive CIE 36-72, July 4, 1975, the field offices of the Customs Bureau have been specifically monitoring the inflow of PCBs and this information is forwarded to EPA. The information is not public.

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APPENDIX A

PCB ADSORPTION TESTING BY XAD-4 RESIN

Experiments and Results

The apparatus and materials used by Rohm and Haas were:

Two glass columns - 1/2 inch in diameter
Adsorbent volume - 50 ml in each column
Adsorbent bed height
XAD-4 Amberlite polymeric adsorbent - 16.5 inches
Activated carbon (Filtrasorb 300) - 15 inches
PCB material used - Aroclor 1254 (manufactured by Monsanto)

A feed solution representing a PCB contaminated waste stream was prepared containing approximately 160 ppb of PCB. Because Aroclor 1254 is very viscous, it was solubilized in methanol prior to dispersion in water. Methanol increases the solubility of PCBs in water. In order to maintain a constant flow throughout the experimental run, two batches of feed solution had to be prepared. The composition of each solution is presented in Table A-1.

Table A-1

Composition of Feed Solutions

Feed Solution A - 13.25 liters
0.0022 gm of PCB or 166 ppb
2 ml of methanol or 119 ppm

Feed Solution B - 13.25 liters
0.0029 gm of PCB or 218 ppb
2 ml of methanol or 119 ppm

The influent solution was passed simultaneously through the column of Amberlite polymeric adsorbent and the column of activated carbon at a flow rate of 2 bed-volumes per hour (0.25 gpm/ft^3 resin). Samples were collected from each column daily, so that each sample nominally represented 48 bed volumes of

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effluent. Liquid passed through both columns for five days, or until 240 bed volumes of effluent (12 liter total volume) were collected from each column.

Prior to analysis, the PCB in each effluent sample was extracted into a volume of hexane equal to one-tenth the volume of the original sample. The influent material, which was sampled four times during the run, was likewise extracted into the same proportion of hexane. This single stage extraction removed more than 95 percent of the PCBs present in the aqueous samples. The extracted effluent samples were then evaporated to 5 mls, further concentrating the PCBs present. These evaporated samples were then sent to Versar Inc., for analysis. The results are given in Table A-2.

Table A-2

Reductions of PCB (Aroclor 1254) Concentrations Through Use Of Amberlite Polymeric Adsorbents and Activated Carbon

Day	Nominal Throughput (BV)	Influent Concentration (ppb)	Effluent Concentration (ppb) Amberlite Adsorbent	Carbon
1	1-48	25 (Feed A)	0.246	0.050
2	49-96	none detected	0.031	0.055
3	97-144	21.1 (Feed B)	0.023	0.025
4	145-192	0.69	none detected	none detected
5	193-240	0.69	3.478	0.045

A significant amount of PCB was adsorbed onto the walls of the influent container, as can be seen with Feed A, which originally was prepared with 166 ppb of PCBs. This loss by adsorption on equipment surfaces also has been detected in other tests, and must be taken into account.

Both the Amberlite polymeric adsorbent and the activated carbon reduced the concentration of PCBs in water to less than 0.05 ppb. The higher concentration of PCBs for the first day's passage of effluent through the resin beds could be due to an incomplete conditioning of the beds, resulting in some material leaching out of the resin. The high concentration of PCBs in the last sample from the polymeric adsorbent must be viewed with some suspicion,

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particularly since it indicates an effluent having a concentration higher than that in the influent.

Amberlite polymeric adsorbents can usually be solvent regenerated, because the energy of adsorption is much lower for resins than it is for carbon. Hence, adsorbed solute can be removed simply by passing an appropriate solvent through the resin. Work performed by Musty and Nickles (J. Chromat., 89:185 (1974)) with PCBs and a solution of 10 percent diethyl ether in hexane as a regenerant indicates that 76 percent of the PCBs adsorbed on an Amberlite polymeric adsorbent can be recovered using this mixed solvent. In addition, Rohm and Haas have found that simple alcohols or ketones are effective solvents for these resins. Undoubtedly, a more efficient solvent could be found that would quantitatively remove PCBs from polymeric adsorbents.

Activated carbon, which has a much higher energy of adsorption than do these resins, requires a more energy intensive process of regeneration, such as thermal rejuvenation.

The ability to solvent regenerate Amberlite polymeric adsorbents in situ would provide the advantage of generating only the more-readily-handled-by incineration liquid phase PCBs wastes.

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APPENDIX B

MACRORETICULAR RESINS FROM ROHM AND HAAS CO.

Description

Ion exchange resins have the capacity to selectively recover ionic constituents, both inorganic and organic, from water through an ion exchange mechanism. Organic compounds are often exchanged or adsorbed irreversibly onto an ion exchange resin. This may cause a decrease in capacity so that the operating life of the resin is diminished. The more recently developed macroreticular type of ion exchange resins are polymeric adsorbents used specifically for adsorbing aromatic and aliphatic compounds from water.

Structures

The macroreticular structures are characterized by having unusually large surface areas as compared with those of conventional gel structures.

Using the newer macroreticular polymerization technique, it is possible to widely vary the particle pore size, pore size distribution, and surface area. Polymers with very small pores (5 nm or less) and high surface areas (in the range of 800 square meters per gram) can be prepared. At the other end of the spectrum, pore sizes on the order of 30 micrometers, visible under modest magnification, are possible.

The macroreticular polymerization technique is applicable to a wide variety of monomers. It is possible to introduce functional groups onto the surface of the preformed macroreticular polymers. Thus, a great range of surface types is possible, limited only by the availability of monomers or the applicability of reactions to introduce functionality. The full line of macroreticular adsorbents constitutes a spectrum of surfaces from the least polar to the most polar. For PCBs removal, the nonpolar and intermediate polarity adsorbents should be used. The chemical structure of Amberlite XAD-2 and Amberlite XAD-4 (see Figure B-1) is representative of the nonpolar adsorbent series. Figure B-2 shows the acrylic-ester composition of Amberlite XAD-7 and Amberlite XAD-8, the intermediate polarity adsorbents. The physical properties of these Amberlite XAD adsorbents are summarized in Table B-1

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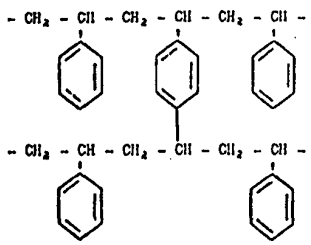

Structure of Amberlite XAD-2 and Amberlite XAD-4

Figure B-1

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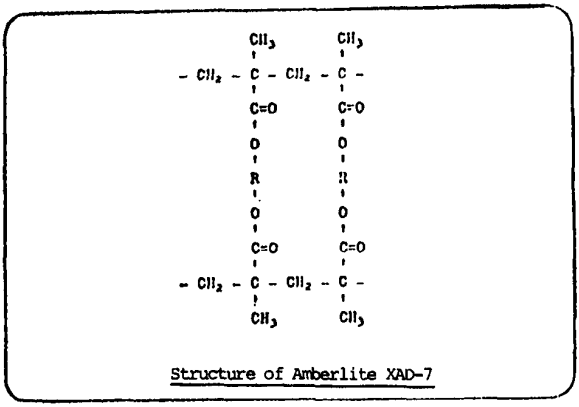
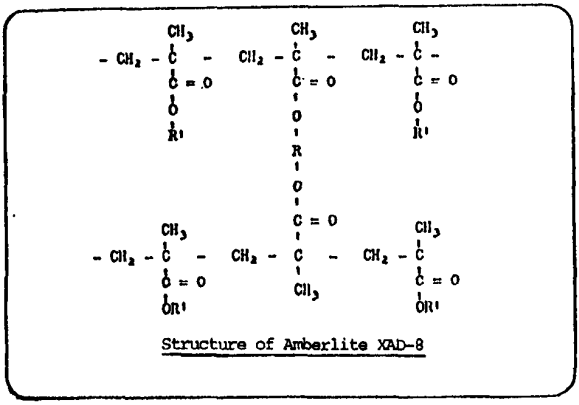


Structure of Amberlite XAD-7



Structure of Amberlite XAD-8

Figure B-2

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Table B-1

Typical Properties Of Amberlite Polymeric Adsorbents

	Chemical Nature	Helium Porosity		Surface Area m^2/gram	Average Pore Dia. Angstroms	Skelatal Density grams/cc	Nominal Mesh Sizes
		Volume %	cc/gram				
Nonpolar							
XAD-1	Polystyrene	37	0.69	100	200	1.06	20 to 50
XAD-2	Polystyrene	42	0.69	330	90	1.08	20 to 50
XAD-4	Polystyrene	51	0.99	750	50	1.09	20 to 50
Intermediate Polarity							
XAD-7	Acrylic Ester	55	1.08	450	80	1.25	20 to 50
XAD-8	Acrylic Ester	52	0.82	140	250	1.26	25 to 50

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Macroreticular Adsorption Phenomena

An important aspect of the Amberlite adsorbents is the nature of the different surfaces. The phenomenon of adsorption on solids involves van der Waals' forces which bind the adsorbate on to the solid surface. Many types of interactions, such as hydrophobic bonding, dipole-dipole interaction and hydrogen bonding, are important. It is not possible to predict accurately which materials will be adsorbed well by a given adsorbent; however, from a practical point of view, a useful concept is that hydrophobic or nonpolar molecules or portions of such molecules are attracted to hydrophobic surfaces, while hydrophilic or polar materials are attracted to hydrophilic or polar surfaces. Examples of these interactions are presented in Figure B-3. If each organic molecule is thought of as having both a hydrophobic and a hydrophilic end, then the hydrophobic end will be attracted to hydrophobic adsorbents such as Amberlite XAD-2 and Amberlite XAD-4, while the hydrophilic end will be attracted to hydrophilic adsorbents. This type of reaction is particularly true when the adsorption takes place from aqueous solution.

For PCBs, it would be expected that the biphenyl portion would be typically aromatic and hydrophobic, and thus attracted to an aromatic resin. Increasing the chlorination of a biphenyl would reduce its water solubility and thus reduce what little polar character the PCB might have. Thus, the PCB would not have a "polar end" and would be strongly repelled by the water phase and strongly attracted by the resin.

A recent study by James Fritz, et al, of Iowa State University, reported a macroreticular resin method for extracting trace organic contaminants from water. He also demonstrated the feasibility of selective desorption of these contaminants, using appropriate eluants, so that the contaminants could be identified. He also established the performance or retention efficiency of the resin in isolating these compounds. A summary of these results is given here:

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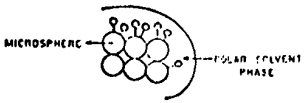
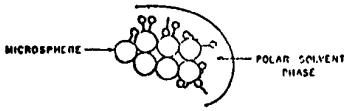
SORPTION ON AROMATIC SORBENTS FROM POLAR SOLUTIONS



SORPTION ON ALIPHATIC SORBENTS FROM POLAR SOLUTIONS



SORPTION ON ALIPHATIC SORBENTS FROM NON-POLAR SOLVENTS

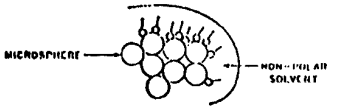


Figure B-3

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Adsorbent: Amberlite XAD-2 unless otherwise indicated

Particle Size: 100 to 150 mesh

Flow Rate: 10 BV/hr. (1.25 gpm/ft^3 of adsorbent)

Test Compounds	Influent	Effluent	Retention Efficiency %
Benzene	100	0	100
Benzene sulfonic acid	3.0	2.1	31
Phenol	0.4	0.22	45
Phenol (Amberlite XAD-7)	0.4	0.06	86
Aniline (Amberlite XAD-7)	4.0	0	100
Naphthalene	0.05	0	100

It can be seen that Amberlite XAD-2 and Amberlite XAD-7 were 100 percent efficient in recovering the nonionic organic compounds. These results predict good success with PCB adsorption. On the other hand, ionic solutes as well as strongly ionized compounds, such as benzene sulfonic acids and p-toluene sulfonic acids, were not retained with the same high efficiency. It was noted that retention efficiency of a contaminant increases with increasing molecular weight in a homologous series, indicating that the higher chlorinated PCBs would be the best adsorbed.

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APPENDIX C

NON-CARBON ADSORBTION AND OTHER RESEARCH STAGE
PCB TREATMENT TECHNOLOGIES

1.0 POLYVINYL CHLORIDE (PVC) AND POLYURETHANE FOAMS

John Lawrence and co-workers of Environment Canada have reported preliminary tests using PVC, polyurethane foams, carbon, and the XAD resins for removal of PCBs from both synthetic wastewater solutions and actual raw sewage.

H. D. Gesser (in Analytical Letters 12:883 (1971)), reported that a polyurethane foam column quantitatively adsorbed PCBs from water. Lawrence found that carbons, polyurethane foams and XAD-2 strongly adsorbed PCBs from aqueous solutions, but were much less effective with raw sewage. He found that PVC, however, was very effective in removing PCBs from raw sewage.

Dr. Lawrence is the only investigator known to have worked with PVC for adsorbing PCBs. Following is a summary of his test procedures and results.

1.1 Experimental Method for PCBs Adsorption Tests, by Environment Canada

Two stock solutions of Aroclor 1242 and 1254 were prepared by vigorously mixing an excess of each Aroclor with water for 8 hours, allowing the solutions to stand overnight and carefully decanting off the true aqueous phase. The water used was double distilled, the second distillation being from an all-glass system. The concentration of these solutions, determined by gas chromatography, was 45 $\pm$ 10 ppb, which is consistent with the published solubility for Aroclor 1254 of 56 ppb.

All solvents used were glass distilled pesticide grade (Caledon Laboratories, Inc.). The activated carbons employed were lignite-based hydrodarco 400 (ICI-United States) and anthracite-based Filtrasorb 400 (Calgon Corporation). These were pretreated by heating to 300°C for 12 hours, cooling, and twice extracting each 500 gm with 2 liters of hexane. The extracted carbon was then filtered and air dried. The polyurethane foams used were DiSPo plugs (Canlab Supplies Ltd.) and Foams 1115 and 2328 (B.F. Goodrich Ltd.). (The first

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two digits in the Goodrich products relate to the density, i.e., 1.1 and 2.3 lb/ft^3 and the second two digits to the hardness). The foams were shredded and successively washed with n-hexane (several times), acetone and distilled water. They were then air dried. This pretreatment was developed to remove trace organic contaminants from the surface of the foams. The macroreticular polystyrene resins Amberlite XAD-2 and XAD-4 (Rohm and Haas Company) were pretreated by successively washing each 500 gm of resin with 1-liter batches of water, methanol, and water. The cleaned resins were stored in sealed glass containers under methanol to prevent them from drying. Polyvinyl chloride chips (Monsanto Company) were washed several times with n-hexane and air dried.

To determine the adsorption characteristics, 100-ml aliquots of stock Aroclor solutions were stirred rapidly for 30 minutes with weighed amounts of adsorbent and then the adsorbent was removed by filtration through a Millipore prefilter pad. Five milliliters of n-hexane were then vigorously stirred with the filtrate for 45 minutes and the organic extract withdrawn. These extracts were analyzed with a gas chromatograph (Varian series) equipped with an electron capture detector (Ni^{63}). The gas column (1.8m x 1.5 mm i.d.) was packed with 4 percent OV-101 and 6 percent OV-210 on Chromosorb W HP $^{80}/_{100}$ mesh. Nitrogen was used as a carrier gas at 50 ml/min. The injection port, column and detector temperatures were 250°C, 200°C, and 300°C, respectively. Extraction and analysis of water samples spiked with known amounts of Aroclor indicated that greater than 98 percent of the PCBs were detected by this method.

Wastewater was collected from the Hamilton Sewage Treatment plant at the raw sewage inlet pipe. Sampling was carried out using all-glass containers to insure against adsorption of PCBs onto container walls. The samples were stored at a constant temperature of 3°C and in all cases were treated and/or extracted within 24 hours of collection. In the evaluation of PCB adsorption from sewage, the procedure described above for pure Aroclor solutions was followed, except that 100-ml samples of raw sewage were stirred vigorously with the adsorbent for 1 hour, and then the adsorbent was separated by filtration through a 60 mesh, stainless-steel screen. After washing, the screen did not retain any raw sewage and, with the exception of activated carbon, 100 percent

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separation of adsorbent was achieved. The filtrates were then twice extracted with 50 ml of n-hexane in 500-ml separatory funnels. The aqueous portion was discharged and the organic phase, after being dried through 15 g of Na_2SO_4, was reduced in a rotary evaporator to approximately 3 ml. The sample was purified by liquid-solid chromatography on a florisil support column using petroleum ether to elute the PCB fraction and then the eluate was evaporated to 3 ml. Prior to injecting the sample into the gas chromatograph, it was shaken with 0.2 ml of mercury to remove residual sulfur compounds.

The PCBs in the samples were identified by comparison of their chromatograms with chromatograms of standard Aroclors. The total concentrations of PCB in raw sewage usually averaged 9.8 $\pm$ 4 ppb.

1.2 Experimental Results of PCBs Adsorption from Sewage and Synthetic Wastewater

Adsorption data for Aroclor 1254 and 1242 on PVC, activated lignite carbon, anthracite carbon, two polyurethane foams, and Amberlite XAD-2 and XAD-4 resins are shown in log-log form in Figure C-1. The weight of PCB adsorbed per unit weight of adsorbent is expressed as a function of the equilibrium concentration of PCB remaining in solution. The sets of data do not follow any of the common isotherm expressions (e.g., Langmuir, Freundlich, BET), and consequently a theoretical interpretation of the results has not been attempted. It is evident that the two carbons and XAD-2 have the greatest adsorptive capacities; however, a residual concentration of less than 3 ppb could not be obtained with lignite carbon. Both polyurethane foams appear to be good adsorbers, with relatively high adsorptive capacities and low residual levels. DiSPo polyurethane foam plugs are also evaluated but these have identical adsorptive properties to the Goodrich Foam 1115. The lower efficiency of XAD-4 is surprising in view of the similarity between it and XAD-2 (they differ only in pore diameters: 9 nm for XAD-2 and 5 nm for XAD-4). The lower efficiency of PVC, which has no macroreticular structure, can be explained by its lower surface area. The surface area per unit weight is reported as 500 to 2000 m^2/gm for carbon, 750 m^2/gm for XAD-4, and 330 m^2/gm for XAD-2, but only 2×10^{-3} m^2/gm for PVC chips - there being no macroreticular structure in PVC. This gives an area ratio for XAD-2/PVC of approximately 10^5.

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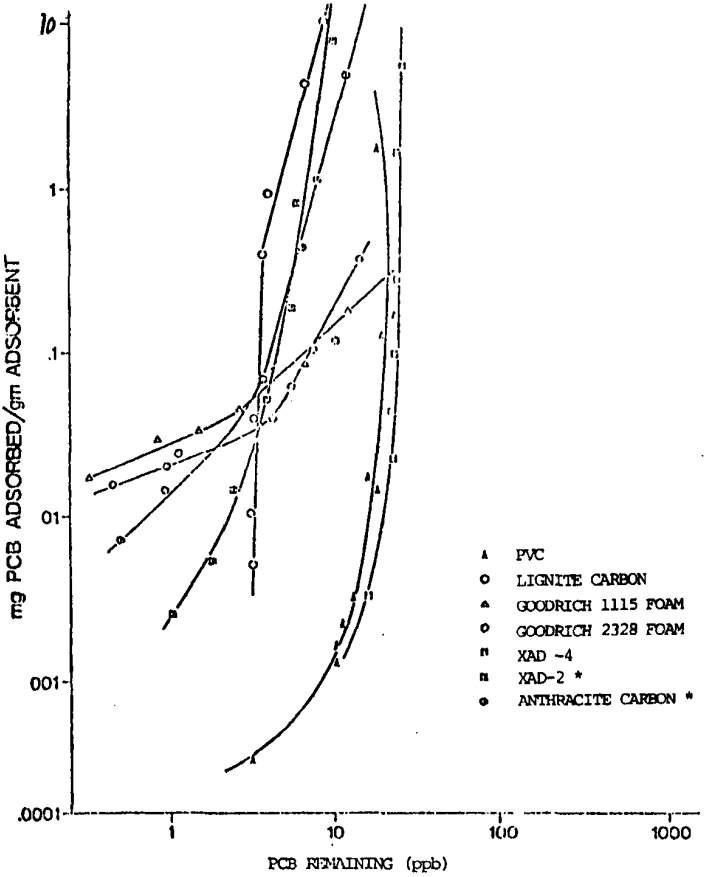

Figure C-1. Adsorption of Aroclor 1254 on P.V.C., Lignite Carbon, Anthracite Carbon, Polyurethane Foams and Amberlite XAD-2 and XAD-4.
* Indicates adsorption of Aroclor 1242 rather than 1254

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There are two complicating conditions associated with adsorbing PCBs from raw sewage rather than from synthetic aqueous solution: (a) sewage contains other hydrophobic organic matter which competes for the active sites on the adsorbent, and (b) much of the PCB has already adsorbed onto the suspended solids by the time the sewage reaches the treatment plant. Condition (b) can be demonstrated easily by filtering raw sewage and monitoring the change in PCB concentration. With typical raw sewage containing 10 ppb PCB, vacuum filtration through a Millipore prefilter pad results in the removal of about 75 percent of the PCBs. It is therefore necessary to find an adsorbent which is not only relatively specific to PCBs, but which also has sufficient affinity for the PCBs to reverse the PCB-suspended-solid equilibrium.

Table C-1 shows the percentage of PCB (including both Aroclor 1254 and 1260) adsorbed from raw sewage by five different media. With the exception of the PVC, approximately 1 gm of each media was stirred with 200 ml of raw sewage for 45 minutes; approximately 10 gm of PVC were used to compensate for its lower surface area. To minimize the inconsistency of raw sewage, the data have been averaged over several determinations on different days and with different sewage samples. The data indicate that PVC and XAD-4 are more effective than carbon or polyurethane foams in terms of percentage of PCB removed from raw sewage. This is surprising since the graphs for PCB adsorption for pure Aroclor solutions (Figure C-1) predict the opposite. Lawrence believes the reasons for this apparent anomaly are: (a) the active sites on carbon are preferentially occupied by hydrophobic species other than PCBs in the sewage, and (b) suspended solids adhere to the surface of carbon and foam acting as a barrier to further adsorption. These results indicate that PVC is superior to the other media for removing PCBs from sewage.

Lawrence's work is continuing, with studies of methods of scale-up and continuous or multistage operations with PVC. Optimum retention time, and methods for continuous addition of fresh PVC and removal of spent PVC are under study.

The strong competition between organic solids and non-organic media is emphasized further in the following discussion.

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Table C-1. Adsorption of PCBs from Raw Sewage

ADSORBENT	% PCB ADSORBED*
Lignite Carbon	46
Polyurethane Foam	35
Amberlite XAD-2	23
Amberlite XAD-4	60
PVC	73

* Includes both Aroclors 1254 and 1260. Data are averaged over several determinations to minimize the variations in raw sewage.

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1.3 PCBs Adsorption on Clays and Organics in the Soil

E. S. Tucker and co-workers at Monsanto reported on studies of migration of PCBs (Aroclor 1016) through various soils as induced by percolating water (Bulletin of Environmental Contamination and Toxicology 13 (1):86 (1975)). The results were to be used for estimating PCBs leached from landfills. Their tests first led them to believe that the higher the clay content of a soil, the better its retention of PCBs.

The experimental procedure employed consisted of percolating water through a column packed with soil coated with Aroclor 1016 and then monitoring the effluent water for PCBs. The soil columns employed were approximately 3 inches in diameter by 12 inches high, and were dry packed in layers. Each soil layer was 3 inches thick, with the first layer being uncoated soil, followed by a layer coated with 2.5 percent (w/w) of Aroclor 1016, and then another layer of uncoated soil. An acetone solution of Aroclor 1016 was used to coat the air-dried soil, followed by removal of the acetone in a rotary evaporator.

Three different types of soils were used in this study. The characteristics of each are shown in Table C-2. The intent was to simulate the various soil types which could be encountered at different landfill sites. The soil types and the procedure employed have been used previously to evaluate the soil mobility of agricultural chemicals.

Distilled water was fed from a reservoir at a constant pressure to each soil column. The effluent flow rates were observed to increase the first few days, then decrease, and finally level out. Apparently, after the wetting phase some channeling occurs until the soil becomes compressed in the column. This effect was most pronounced with the silty soils. The average flow rates for Norfolk Sandy Loam, Ray Silty Loam and Drummer Silty Clay Loam were 0.26, 0.53 and 0.32 liters per day, respectively. The effluents then were quantitatively adsorbed on polyurethane columns, then extracted and analyzed by electron capture gas chromatography.

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Table C-2

COMPOSITION OF SOILS USED IN THE MONSANTO STUDY

Soil	Norfolk Sandy Loam	Ray Silty Loam	Drummer Silty Clay Loam
% Sand	82.5	6.2	2.8
% Silt	11.0	83.2	55.4
% Clay	5.5	9.6	35.8
% Organic Carbon	1.0	1.0	6.0

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1.3.1 PCBs Adsorption Results

PCBs adsorption results are given in Table C-3. These results indicate that clay was a strong adsorbent for PCBs. This would be in agreement with the work of R. Hague and co-workers (Environmental Science Technology, 8:139 (1974), in which clay was found to have a high affinity for PCBs. However, in later work with pure clays, the retention was found not to be as good as expected. Attention was then directed to the organic portion of the soils, and Tucker, et al, have tentatively decided that the organic fraction is more important to the adsorption of PCBs; it can be seen from the data that the high-clay-content soil was also the high-organic-content soil.

Further investigation of some clays might be warranted. S. Pearson of Hercules, Inc., in a personal communication, stated that bentonite clay was very effective in removing other pesticide wastes from water. The finely divided clay was then rapidly removed from the water with "Hercofloc".

1.4 Spahgnum Peat (Lignin-Cellulose) as an Adsorbent

The above work by Tucker, and the general finding that in sewage sludge the solid phase contains many times the amount of PCBs the water phase contains, leads to the conclusion that natural organic materials from the earth might make good adsorbents for PCBs.

Although it has not yet been tested for removing PCBs, there is a commercial method of continuous wastewater treatment, called the Hussong/Couplan Water Treatment System, that uses sphagnum peat. The peat is formed into a continuous mat on a mesh belt through which wastewater is sprayed. The system has shown high effectiveness in removing certain organics and metals from wastewaters.

Capital costs for this system average about 60¢ per gallon of daily capacity. Operating costs, when treating a dye house effluent, were 7¢ to 14¢ per 1000 gallons.

2.0 CATALYTIC REDUCTION

In the literature review, two approaches were found for modifying the chemical structure of PCBs in order to aid in waste control. One approach was the

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Table C-3

PCBs FOUND IN PERCOLATING WATER

Norfolk Sandy Loam		Ray Silty Loam		Drummer Silty Clay Loam	
Total Effluent Volume (ℓ)	ppb PCBs	Total Effluent Volume (ℓ)	ppb PCBs	Total Effluent Volume (ℓ)	ppb PCBs
1.3-8.1	ND	2.7-16.4	ND	1.6-9.9	ND
10.1	ND	20.7	65	12.5	ND
13.5	23	27.6	92	16.6	ND
25.5	63	51.9	153	31.4	ND
48.1	63	98.1	136	59.2	ND

ND = None detected, < 1 ppb

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complete chlorination of PCBs, to give decachlorobiphenyl, the rationale being that the completely chlorinated biphenyl would have the least solubility in water of any PCB, and thus would be much easier to adsorb and remove. However, decachlorobiphenyls are also the most refractory PCBs.

A better approach is the dechlorination of PCBs to give biphenyl or bicyclohexyl. Berg, et al (in the Bulletin of Environmental Contamination Toxicology 7:338 (1972) state that PCBs can be dechlorinated quantitatively with hydrogen over platinum or palladium catalysts to give bicyclohexyl.

T. Sawai of Japan (in Genshiryohu Kogyo 18(12):43-7 (1972)) reported the degradation of PCBs using the cobalt 60 isotope. Gamma irradiation at a level of 10^{18} ev/gram produced chain dechlorination in an alkaline propanol solution saturated with nitrogen. Alkaline concentrations of 0.01 molar gave about 40 times the dechlorination that a neutral solution gave.

A process of reductive dechlorination, more amenable to low-cost operation and commercial scaleup, is being developed by Sweeny, Saltonstall and co-workers at Envirogenics Systems Co. of El Monte, California.

2.1 Reductive Dechlorination of PCBs at Envirogenics Systems Corp.

Envirogenics, originally working in chlorinated pesticides, has developed catalyzed reduction process methods for the following compounds:

DDT	aldrin	Aroclor 1221
DDD	Chlordane	Aroclor 1242
Kelthane	dieldrin	Aroclor 1254
Perthane	endrin	Aroclor 1232
Methoxychlor	heptachlor	Aroclor 1248
Lindane	toxaphene	Aroclor 1260

The reductive dechlorination reaction has been run at ambient temperature and pressure, by flowing the liquid chlorinated hydrocarbon through a column containing metallic iron granules coated with a metallic copper and blended with sand. The copper exerts a catalytic action. pH is maintained at nearly neutral, since with low pH, say 2.0, the iron conversion rate to ferrous chloride increases 10 times, but the dechlorination reaction is not much faster. The chlorinated hydrocarbon is converted to a hydrocarbon. PCBs, in this process, seem to lose chlorines stepwise, leaving unidentified PCB homologs.

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Envirogenics is now under EPA contract (68-03-2364) to develop and demonstrate an effective bench-scale (1-3 gpm) low-cost process for the treatment of dilute (ppb to 1 ppm) aqueous manufacturing and processing wastes containing PCBs. Specific objectives and guidelines include:

1. Reduction of PCBs to 5 ppb or less, with levels of < 1 ppb desirable
2. Sufficiently low projected treatment cost to be economically attractive
3. Low expected toxicity of all effluent products, including both degraded PCBs and any added reagents
4. Use of readily available materials, both in construction and as reagents

The process entails simply pumping the liquid to be treated through the catalytic column. Process characteristics that might be proposed for the scaled-up PCB operation, based on what has been learned about the other pesticides thus far, are:

catalyst: 100-mesh metallic iron granules coated with 0.1 milliequivalents of copper per gram of iron

support: 60 to 100 mesh (approx.) sand

number of beds: 4, operable in series or parallel

bed composition: 500 pounds of iron catalyst, plus 3500 pounds of sand

flow rates: 2 to 10 gpm /ft^2

pressure drop: about 10 psi

pH: kept neutral, through caustic addition

piping: 304 ss, with teflon tape seals

tanks: Steel with epoxy coating inside

pretreatment: Wastes are assumed to be free of undissolved solids and oils and are fabric filtered before entering process

The expectations for wastewater PCB reductions with such a pilot plant are based on small 1- to 2-inch-diameter column lab tests that gave reductions of PCBs from 50 ppb to less than 0.1 ppb.

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The capital cost of the equipment to process 100 gpm is estimated at $65,000, plus tank storage and construction costs. Operating costs, including amortization of capital, is estimated at 72¢ per 1000 gallons of effluent.

3.0 CATALYTIC OXIDATION AND MISCELLANEOUS REACTIONS

The catalytic oxidation of PCBs includes oxidation by: air, oxygen, ozone, hydrogen peroxide and chlorine dioxide. The reaction is usually assisted by catalysts or reaction sensitizers.

PCBs are very resistant to chemical attack. Monsanto states that they are not affected by boiling sodium hydroxide, or by long contact, say 10 days, with concentrated sulfuric acid at ambient temperature. There is no apparent reaction in a bomb of oxygen at 250 psi and 140°C.

3.1 Strong Acids

Russian workers have reported nitric acid decomposition of PCBs. They used nitric acid at a specific gravity of 1.4, and refluxed two PCBs, a pentachloro and a heptachloro homolog, for periods ranging up to 100 hours. They found di- and trichlorobenzoic acids from the former, and tri- and tetra chlorobenzoic acids from the latter. Less concentrated nitric acid would not oxidize these compounds, nor would potassium permanganate or chromic acid. However, mono-, di- and trichlorobiphenyls can be oxidized to the corresponding chlorobenzoic acids with chromic anhydride and acetic acid. The less rigorous conditions can also produce a large mixture of nitrated chlorobiphenyls.

3.2 Electrochemical Oxidation

Notwithstanding these examples of oxidative resistance, J. D. Stuart and co-workers at the Dept. of Chemistry of University of Connecticut have conducted laboratory electrochemical oxidations of PCBs at ambient temperature and pressure. They oxidized PCBs having one to ten chlorine atoms, using very high anodic potentials in a dry methylcyanide solvent. They hypothesize a series of reactions starting with hydrolysis from traces of water present and ending with oxidation.

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A number of other catalytic oxidation investigations of refractory organics are being conducted in the U.S., with some being sponsored by EPA. Although PCBs have yet to be tested in these investigations, the methods have sufficient power and flexibility to indicate PCBs could be destroyed. In addition, these methods have the potential for zero discharge of pollutants since they have converted refractory organics to CO_2 and water.

3.3 Catalytic Ozonation and Ultrasound Decomposition of Organics

Gerard Smith and J. W. Chen of Southern Illinois University have presented results (68th annual AIChE Meeting in November, 1975) of catalytic ozonations of non-PCB organics in aqueous systems. They have tested catalysis with oxygen, and ozonation without catalyst, and neither method had the effectiveness of catalytic ozonation. An Fe_2O_3 catalyst was used, and phenol and ethyl acetoacetate were used as model compounds in water. The liquid retention time in their flow reactor system was 25 minutes, and the gas flow (using 30 mg/liter concentration of ozone) was 0.1 liter per minute. Under these conditions, TOC was decreased 95 percent for an initial TOC of 100 mg/l, and 85 percent for an initial TOC of 400 mg/l. The packed reactor had the aqueous solution flowing down, and the ozone flowing up.

In experiments comparing the effectiveness against refractory organics of ozone plus Raney nickel and ozone plus ultrasound, Smith found that the reactions were similar. Also, he found that ultrasound and oxygen gave similar reactions. Ultrasound was applied at 800 KHz, and 4 to 5 watts per cm^2. It appeared, however, that these effects were not additive; for example, adding ultrasound to an ozone catalytic reaction did not materially change the reactivity of the ozone and catalyst alone. He also found that at these ambient temperatures and pressures, phenol disappeared rapidly, but other organics, including oxygenated aromatics, resulted rather than compounds expected from rupture of the aromatic ring.

3.4 Wet Catalytic Oxidation of PCBs

L. W. Ross at Denver Research Institute has studied the wet catalytic oxidation of strong wastewaters having COD values of 3,000 to 15,000. Tests

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showed that reacting $Fe_2(SO_4)_3$, Cu SO_4, and H_2O_2 at a pH of 5.0, and Fenton catalyst at a pH of 2.5 reduced COD concentrations by 95.4 and 96.0 percent respectively after 2 hours at 400°F. Platinum oxide as a solid catalyst also gave good results. Most of the organics were cellubiosics.

3.5 Wet Catalytic Oxidation and Catalyst Durability

J. F. Katzer and co-workers at University of Delaware have been studying elevated pressure and temperature catalytic air-oxidation of refractory organics. They are currently being supported by EPA in a study of the durability of catalysts in wastewater environments. In a paper soon to be published in the Journal of the Water Pollution Control Federation, Katzer reports on studies of the complete oxidation of phenol to CO_2 and water in an aqueous medium using a supported copper oxide catalyst. Rapid degradation rates were found, and the rate data were used to run preliminary design and costs for commercial-scale waste treatment plants. His conclusion is that catalytic oxidation of wastewaters is cost competitive with other physical chemical treatment techniques.

Katzer found that pressures of 10 to 20 atmospheres, and temperatures of 100 to 200°C, were required to get adequate reaction rates yielding up to 99 percent conversion of organics to CO_2 and water. It was found that ambient temperature and pressure generally caused more adsorption on a variety of catalysts than did any reaction.

3.6 Dye-Sensitized Visible Light Photo-Oxidation of Organics

R. L. Sanks and co-workers at the Civil Engineering Dept. of Montana State University are working on the dye-sensitized, aerobic, photo-oxidation of refractory organics. They were able to rapidly break apart the benzene ring of cresol using such dyes as methylene blue and bengal rose. The key to the process is that in the presence of sunlight and air, methylene blue can produce singlet oxygen from the O_2 in air. There are two forms of this singlet oxygen, with a half life of only a millisecond, but with the ability to easily shatter benzene rings. Sanks visualizes a process whereby a lagoon containing wastewater with refractory organics, could have the dye molecules attached to a long chain alkyl

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or a floc of some kind to keep them at the surface. The sun would provide the photolysis, and little dye would be consumed as it is a catalyst in the reaction. Such a process, if it can be developed, suggests a route to a very low-cost method of obtaining zero discharge, and water recycle systems.

3.7 Chlorine Dioxide Oxidation

International Dioxide, Inc., of New York City is offering a stabilized chlorine dioxide, which is being used by municipalities for taste and odor control of water. It is used as an adjunct to chlorination and can decompose chloramines. It oxidizes and destroys phenol and does not chlorinate. Unstabilized ClO_2 is a dangerous explosive, thus stabilization offers a very powerful oxidizing agent for potential degradation of organics.

4.0 DESTRUCTION OF PCBs BY MICROORGANISMS

The Chemistry of PCBs by Hutzinger reports only two pure cultures of microorganisms showing metabolic activity on individual chlorobiphenyls. One culture, Rhizopus japonicus only converted the mono- or dichlorobiphenyls to chlorohydroxybiphenyls or possibly multi-hydroxybiphenyls.

More promising results were obtained with two species of achromobacter, isolated from sewage effluent. Under aerobic conditions, 4-chlorobiphenyl was converted to 4-chlorobenzoic acid. The organism was apparently able to attack the nonchlorinated benzene ring. Most of these degradations take a number of hours to occur. More recently, chlorinated biphenyls up through pentachlorobiphenyl have been oxidized by achromobacter. Monsanto was able to demonstrate a significant reduction in the mono-, di, and trichlorobiphenyls of Aroclor 1242 after 72 hours of treatment with activated sludge. The higher chlorinated homologs did not seem to be affected.

The degradation of PCBs by microbial action from sludges and from pure cultures of bacteria seemed to give results similar to animal metabolism studies. The lower chlorinated species, again up through the trichloro homolog, were decomposed to phenols, catechols and related compounds.

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The importance of oxidative conditions was demonstrated in tests with silage containing PCBs. After several months of storage of Aroclor 1242 with silage that had undergone fermentation reactions under anerobic conditions, no change in any of the PCBs had taken place.

The use of DDT degradation as a model for PCB degradation conditions may not be helpful. Results of a study by Johnsen (PCB Newsletter, January, 1973) showed that when di- to hexachlorobiphenyls were incubated for one month with soil and with soil containing cattle manure, no indication of PCB metabolism was found. Under these conditions, p,p' DDT degrades almost completely.

It has also been found that biphenyl itself is more easily degraded or hydroxylated than any of the chlorinated biphenyls.

5.0 REVERSE OSMOSIS AND ULTRAFILTRATION

No tests for PCBs removal by reverse osmosis or ultrafiltration were found in our literature survey. Generally, these methods have found most success in removing dissolved salts from water. However, E.I. DuPont reports, in a private communication, that they have achieved 90 percent removal (rejection) or organics in water at the 1000 to 2000 ppm level. They accomplished this through the development and use of a hollow-fiber permeator system having fibers of aromatic polyamides. The system is reported to work well on organics having molecular weights greater than 100. This would indicate probable success with the PCBs, all of which have molecular weights in the range of 200 to 400.

Based on their experimental work with wound polyamide membranes operating on chlorinated hydrocarbons in water, U.O.P.'s Fluid System Division predicts a 95 to 97 percent removal of aqueous PCBs at 50 ppb concentrations. They point out however, that the reject water stream of concentrated PCBs would contain 10 to 20 percent of the original volume of wastewater so that a certain amount of recycle would have to be built into the system to reduce the generation of concentrated wastewater. Reverse osmosis systems cannot tolerate suspended solids in the feed wastewater; under optimum conditions they can operate for six month to one year before any maintenance or cleaning is required.

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W. L. Short of the Chemical Engineering Dept. of the University of Mass. reports that with ultrafiltration, 50 percent rejections of phenols and chlorinated phenols has been achieved. He believes that rejection of a given compound can be improved by attaching some of that compound, or a similar material, to the membrane to act as an electronic barrier.

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APPENDIX D

MASS BALANCE MODEL FOR PCB DISTRIBUTION

1.0 INTRODUCTION AND MASS BALANCE EQUATION

In order to discover the effect of various possible regulatory efforts on the distribution of refractory organics in the general environment, an attempt has been made to determine the manner by which a specific group of such compounds, PCBs, has become so widely dispersed, to determine the dynamics of the distribution process and to determine the changes in specific distribution that may be expected to result from several regulatory alternatives. Specifically, the effect of the voluntary ban introduced by Monsanto in 1970-71 can be demonstrated.

It would be most useful to construct a mathematical representation of a suitable segment of the environment based on the existence of large quantities of valid analytical data taken over a sufficiently long time interval so as to allow the reliable extrapolation of the important time effects. Unfortunately, the necessary data are not available. The recognition that PCBs were an environmental hazard came after their prolonged and widespread use in industry. In addition, the ability to analyze environmental samples for very low levels of PCBs is also a recent development. There has been too little time since the development of these sophisticated and exceedingly sensitive analytical techniques to have allowed anything like a complete spatial and temporal study of the levels of PCBs in any given region.

In view of the serious lack of a truly adequate data base, and because of the need to have at least a first order understanding of the physical processes involved in the transport and distribution of PCBs, an attempt has been made to construct a mathematical model which should contain at least a germ of the true situation. Specifically, the model serves to indicate something of the nature of the problem, and of the types of measurements that will be required to construct a truly satisfactory model to guide future regulatory activities.

To make what follows specific, the derived model is applied to a study of Lake Michigan where a considerable body of information, of late origin, is available.

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1.1 Mass Balance Model

In order to construct a mass balance model to be applied to a body of water such as Lake Michigan, it is appropriate to determine the manner in which an incremental increase in PCB content is distributed within the various processes available. In what follows, it is explicitly assumed that:

(a) There are no effective mechanisms for the degradation of PCBs which are operative over the time scale involved.

(b) The PCBs that remain in the body of water are distributed between that portion in solution in the aqueous phase, that in "solution" in the biota and that contained within the sediments.

(c) The essential loss mechanisms are evaporation from the lake surface and carry off due to the outflowing waters (in this case - through the Strait of Mackinac).

In terms of these assumptions, a differential equation can be developed that describes the time rate of change of the concentration in the various phases in terms of the input rate of PCBs. This equation may be integrated under various assumptions as to the time dependence of the input rate to yield alternate expressions for the concentration of PCB within the separate phases as a function of time.

1.1.1 Model Development

Let B(t) be the rate of injection (lb/yr) of the PCBs from all sources at a reference time t [where t (years) = 0 in 1930]. Then, within the interval t to t + Δt, an incremental amount of PCBs equal to B(t)Δt will be injected into the system. This quantity of PCBs will be partially partitioned into the various phases, with the balance removed by evaporation and/or outflow.

If Q(lbs) is taken to represent the total water mass in the Lake (assumed to be constant) and $C_w(t)$ the concentration of PCBs in the water

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at time t, then

$$C_w(t + \Delta t) = C_w(t) + \frac{\Delta C_w}{\Delta t} \Delta t$$

which, in terms of the definition of concentration, causes an increase in soluted PCB of magnitude

$$\Delta m_w = Q \frac{\Delta C_w}{\Delta t} \Delta t. \qquad (1\text{-}1)$$

In a wide variety of environmental situations[1] there appears to exist a rather definite relationship between the concentration of PCBs within the sediment and/or the "average" member of the biota and that of the water in which they are immersed. These relationships are herein defined as

$$\left.\begin{aligned} \rho &\equiv \frac{C_{sed}}{C_{water}} \\ \eta &\equiv \frac{C_{biota}}{C_{water}} \end{aligned}\right\} \qquad (1\text{-}2)$$

and are assumed to be independent of C_{water} and of time.

Using the relationships expressed by Eq. (1-2), the incremental increase in the mass of PCB stored in the biota is given as

$$\Delta m_{biota} = G\eta \frac{\Delta C_w}{\Delta t} \Delta t, \qquad (1\text{-}3)$$

where it is assumed that the concentration of PCB within the biota was in equilibrium with that in the water at time t and that G(lbs), the total mass of the exposed biota, is constant over the period of interest.

Similarily, if the rate of deposition of sediments is taken to be D(lbs/m^2/yr) and the area of the lake to be A(m^2), then, assuming that the principal exchange processes between water and sediment occur within the aqueous phase during the settling out process, the incremental PCB pickup by the sediments is given as:

$$\Delta m_{sed} = AD\rho C_w(t)\Delta t \qquad (1\text{-}4)$$

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[where the additional term $(1/2)\frac{\Delta C}{\Delta t}\Delta t$ is considered small, especially as $\Delta t \to o$].

If the rate of outflow from the lake (through the Strait of Mackinac) is taken as S(lbs/yr), then the loss of PCB due to this outflow may be taken as:

$$\Delta m_{outflow} = SC_w(t)\ \Delta t \tag{1-5}$$

Finally, the mass of PCB carried out of the system by evaporation is given as:

$$\Delta m_{evap} = KC_w(t)\Delta t \tag{1-6}$$

where K is the evaporation rate constant which will be discussed below.

Now, the principle of conservation of mass requires that all the injected PCB be accounted for, (note that no effective degradation processes are considered to be operative) from which it follows that

$$B(t)\Delta t = \Delta m_w + \Delta m_{biota} + \Delta m_{sed} + \Delta m_{outflow} + \Delta m_{evap}$$

Introducing the definitions of each of the incremental mass loads, and proceeding to the limit $\Delta t \to o$ and dropping the subscript w since the only concentration appearing is that of the PCB in water, the operative differential equation becomes

$$(Q + Gn)\frac{dc}{dt} + (S + K + .ADp)C = B(t) \tag{1-7}$$

which, for convenience in what follows, may be rewritten using the substitutions,

$$\left.\begin{aligned} Y &\equiv \frac{1}{Q + Gn} \\ X &\equiv \frac{S + K + ADp}{Q + Gn} \end{aligned}\right\} \tag{1-8}$$

$$\frac{dc}{dt} + XC = YB(t). \tag{1-8^1}$$

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The general solution of Equation (1-8') takes the form

$$C(t_f) = e^{-Xt_f} \int_o^{t_f} YB(t) e^{Xt} dt \qquad (1\text{-}9)$$

where $C(t_f)$ is the concentration of PCB in water at the reference time t_f ($t_f = 0$, 1930).

To solve Equation (1-9), it is necessary to evaluate the various constants [Equation (1-8)] and to discover an appropriate form for the driving function B(t).

2.0 PCB PRODUCTION, SALES AND ENVIRONMENTAL LOAD

In the following section, an attempt is made to evaluate the production and sales of PCBs during the period 1930-1975. Data published by Monsanto[2] have been presented elsewhere in this report. From the derived empirical expression for the total sales as a function of time, as well as from the empirical expressions for transformer, capacitor and other use categories, it will be possible to estimate the total environmental load of PCBs as a function of time. From this analysis, it will be possible to estimate that portion of the total environmental load that is, in fact, free and which therefore is responsible for the widespread distribution of these refractory compounds. As a final step, it will be possible to estimate the time dependence of the free (wild) PCB input to a closed system such as Lake Michigan.

2.1 Empirical Representation of PCB Sales, General and in Specific Use Categories

2.1.1 Period 1930-1970

From the Monsanto sales data for PCBs, it is possible to fit an empirical expression for each category which, to a satisfactory degree, represents the time dependence of that parameter. In each case, it is assumed that the relation is of the general form:

$$\ln Q(t) = a + n \ln t \qquad (2\text{-}1)$$

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(a) Total Production

The derived empirical expression for the yearly production takes the form, for the period 1930-1970,

$$Q_{prod}(t) = 2.94 \times 10^{2} t^{3.428} \text{ lbs/yr} \qquad (2\text{-}2)$$

The appropriate empirical expression for the yearly sales, for the period 1930-1970, takes the form

$$Q_{sales}(t) = 311\ t^{3.39} \text{ lbs/yr} \qquad (2\text{-}3)$$

The corresponding expressions for capacitor sales and for transformer sales are (for the period 1930-1970)

Capacitor sales: $$Q_{cap}(t) = 2.03 \times 10^{2}\ t^{3.289} \text{ lbs/yr} \qquad (2\text{-}4)$$

Transformer sales: $$Q_{trans}(t) = 2.02 \times 10^{3}\ t^{2.37} \text{ lbs/yr} \qquad (2\text{-}4^{1})$$

In the above expressions, it should be noted that it is explicitly assumed that

(a) the given Monsanto data are accurate and represent the great preponderance of PCB production and sales within the U.S.

(b) the trends noted in the interval 1954-1970 are simple continuations of earlier trends, so that the curves which fit the period 1954-1970 can, in fact, be used to cover the entire interval, 1930-1970.

Information reported elsewhere in this report suggests that the second assumption above might result in low estimates for total U.S. sales; therefore, the results derived from this analysis must be considered as a lower bound on the actual situation.

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In any case, numerical evaluation of expressions (2-3) and (2-4) suggest that a weighted average for the proportion of PCB sales that were employed in electrical applications is of the order of

$$\beta = 0.62 \text{ (i.e., 62\%)} \qquad (2\text{-}5)$$

The remainder of the sales during the period 1930-1970 was for non-electrical applications.

2.1.2 Period 1971-1975

In 1970, Monsanto instituted a voluntary ban on the sales of PCBs restricting their use to electrical applications. As a result of this ban, the empirical relationship appropriate for sales in the post 1970 period is

$$Q'_{sales}(t) = 3.31 \times 10^7 \text{ lbs/yr} \qquad (2\text{-}6)$$

In addition, during this period essentially 100 percent of PCB production was used for electrical applications; i.e.

$$\beta = 1.00 \text{ (1970-1975)} \qquad (2\text{-}7)$$

To determine the total sales and total electrical system usage for the period 1930-1975, Equation (2-3) may be combined with Equation (2-6). Integration over the appropriate time frame yields

$$\sum_{1930}^{1975} Q_{sales} = 9.33 \times 10^8 \text{ lbs}$$

and for total electrical system usage, Equations (2-4) and (2-6) with (2-7) may be combined and, on integration, yield,

$$\sum_{1930}^{1975} Q_{electrical}(t) = 7.12 \times 10^8 \text{ lbs}$$

The balance, 2.21×10^8 lbs, were used in non-electrical applications.

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2.2 Environmental Load of PCBs

2.2.1 Introduction

PCBs, or for that matter any other refractory chemical compound, may exist in the environment in two distinct states: (a) that material which is in a form such as to remain localized and thus is not actually available to enter the sensitive portion of the environment, i.e., the biota; and (b) that material which is not so constrained and is thus free to enter the sensitive portion of the environment. This latter portion of the environmental load will be referred to as "free" or "wild" PCBs. The significance of the first category lies in the fact that the containment is not of infinite life and thus material in category (a) can and will eventually become a component of category (b). For those compounds for which there exists relatively high rates of degradation within the environment, the category (a) is of somewhat lesser importance than for those refractory compounds for which the only inactivation mechanism is the entrapment with non-available forms, for example, in deep ocean sediments.

In order to estimate the rate of accumulation of PCBs in category (b), it is first necessary to determine the rate of entry of PCBs into the category (a). This will be followed by an analysis of the processes by which this total environmental load eventually becomes wild PCBs.

2.2.2 Total Environmental PCB Load, $M_{ev}(t)$

It is assumed that, in any time interval t to t + Δt, a fraction $\alpha < 1$ of the total sales during that interval was directly lost to the environment. It is further assumed that a fraction $\beta < 1$ of the total sales was used in the manufacture of long lived electrical components. If the average lifetime of these electrical components (time of service prior to their being discarded as obsolete) is γ_1 years, then during the time interval t to t + Δt, an amount

$$\beta\, Q_s(t-\gamma_1)\, \Delta t \qquad (2\text{-}8)$$

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will enter the environment as part of category (a). In addition, the direct entry is given as

$$\alpha\, Q_s(t)\, \Delta t \tag{2-9}$$

The remaining sales $(1-\alpha-\beta)\, Q(t)$ was used in the production of relatively short-lived products, such as carbonless paper, hydraulic fluids, etc., which are assumed to have an average lifetime γ_2 years. Thus, the entry of this material into the total environmental pool is given by

$$(1-\alpha-\beta)\, Q_s(t-\gamma_2)\, \Delta t \tag{2-10}$$

If the three components of the total environmental load, $M_{ev}(t)$ are summed, the resulting differential equation for $M_{ev}(t)$ becomes, in the limit as $\Delta t \to o$

$$\frac{dM_{ev}(t)}{dt} = \alpha\, Q_s(t) + (1-\alpha-\beta)\, Q_s(t-\gamma_2) + \beta\, Q_s(t-\gamma_1) \tag{2-11}$$

or

$$M_{ev}(t) = \alpha \int_o^t Q_s(t)dt + (1-\alpha-\beta)\int_o^t Q_s(t-\gamma_2)dt + \beta\int_o^t Q_s(t-\gamma_1)dt \tag{2-11'}$$

In order to obtain a numerical evaluation of Equation (2-11') it is appropriate to note that β, the fraction of initial sales utilized for electrical applications, is given by Equation (2-5) for the period 1930-1970, and by Equation (2-7) for the post 1970 period.

An estimate of the factor α, the fraction of direct losses, can be obtained by noting that

(a) approximately 10% of the electrical material was lost during transport, production and processing.[3]

(b) approximately 30% of the non-electrical material was lost during transport, production, processing, and use.[4]

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Hence,

$$\alpha = (0.1)(0.62) + (0.30)(.38)$$
$$\alpha = 0.17 \qquad (2\text{-}12)$$

It is further assumed that

$$\overline{\gamma}_1 = 20 \text{ years}^{(5)}$$
$$\overline{\gamma}_2 = 4 \text{ years}^{(6)} \qquad (2\text{-}12')$$

If the expression of $Q_s(t)$ given by Equation (2-3), coupled with the estimated values of α, β, γ_1, and γ_2, is introduced in Equation (2-11), the total environmental load $M_{ev}(t)$ may be computed. The integrated form of Equation (2-11) is:

$$M_{ev}(t) = 71.07 \left[0.17t^{4.39} + (0.21)(t-4)^{4.39} + (0.62)(t-20)^{4.39} \right] \qquad (2\text{-}13)$$

The numerical results are summarized in Table 2.2.2-1. It should be noted that, in contradistinction to equations such as Equation (2-3), which represent the yearly sales, Equation (2-13) represents the cumulative load in pounds.

2.2.3 Effect of Monsanto's Voluntary Ban on PCB Sales

In the actual situation, as a result of the voluntary Monsanto ban on PCB sales, the expression $M_{ev}(t)$ given by Equation (2-13) must be modified to account for post 1970 levels. Thus, for the period 1971 and later,

$$M_{ev}(t) = M_{ev}(40) + 0.1\int_0^{t-40} Q'(t)dt + (1-\alpha-\beta)\int_{40}^{t-40+\gamma_2} Q(t-\gamma_2)dt$$
$$+ (1-\alpha-\beta)\int_{t=40+\gamma_2}^{t} Q'(t-\gamma_2)dt + \beta\int_{40}^{t} Q(t-\gamma_1)dt \qquad (2\text{-}14)$$

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TABLE 2.2.2-1

$M_{ev}(t)$ = Environmental PCB Load

Date	t(yrs)	Without Partial Ban [From Equation (2-13)] $M_{ev}(t)$ (lbs)	With Partial Ban [From Equation (2-13/2-15)] $M_{ev}(t)$ (lbs)
1930	0	0	0
1935	5	1.42×10^4	1.42×10^4
1940	10	3.35×10^5	3.35×10^5
1945	15	2.32×10^6	2.32×10^6
1950	20	9.1×10^6	9.1×10^6
1955	25	2.62×10^7	2.62×10^7
1960	30	6.23×10^7	6.23×10^7
1965	35	1.31×10^8	1.31×10^8
1970	40	2.54×10^8	2.54×10^8
1975*	45	4.58×10^8	3.76×10^8
1980*	50	7.79×10^8	4.66×10^8

*Equation (2-13) is not actually valid for the post 1970 period, but if the voluntary ban had not been imposed, the estimated $M_{ev}(1975)$ would have been as recorded in Table 2.2.2-1.

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Substitution of the appropriate forms of $Q_s(t)$ and $Q_s'(t)$ and integration results in

$$M_{ev}(t>44) = \frac{\alpha\delta t^{4.39}}{4.39}\Bigg|_0^{40} + \alpha'\delta'(t-40) + \frac{(1-\alpha-\beta)\delta(t-\gamma_2)^{4.39}}{4.39}\Bigg|_0^{44} + \frac{\beta\delta(t-\gamma_1)^{4.39}}{4.39}\Bigg|_0^{t} \qquad (2\text{-}14^1)$$

which, on introduction of the appropriate numerical values [note $\alpha' = 0.1$, i.e., after 1970, the only use of PCBs was in the manufacture of electrical equipment from which some 10 percent of the material used is discarded as scrap]; becomes

$$M_{ev}(t>44) = 2.99 \times 10^8 + 3.31 \times 10^6\ (t-40) + 44.1\ (t-20)^{4.39} \qquad (2\text{-}15)$$

This latter Equation (2-15) has been used to compute the 1975, 1980 entries in the fourth column of Table 2.2.2-1. By comparison of the last two entries in Table 2.2.2-1, the direct effect of the voluntary ban in 1970 becomes obvious.

2.3 Mobile or Free Environmental PCBs, $m_{ev}(t)$

2.3.1 General Considerations on Mobile PCBs

To consider the processes by which the general environmental load of PCBs $\left(M_{ev}(t)\right)$ becomes free, i.e., the processes by which $m_{ev}(t)$ is generated, it is necessary to consider that some fraction of the direct losses are in a form such that the lost material immediately becomes mobile; i.e., spills and/or evaporation losses. Further, the non-mobile material is usually encased or enclosed in some sort of container which will eventually be degraded thus allowing the subsequent escape of the component PCB.

The fraction of the total sales that is waste occuring in all production uses of PCBs is $\alpha Q_s(t)$ of which some fraction ε is directly mobile.

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Thus, in the time interval t to t + Δt, this component introduces an amount

$$\varepsilon\alpha Q_s(t)\Delta t \tag{2-16}$$

into the free environmental pool. The remainder $(1-\varepsilon)\alpha Q_s(t)$ which enters the environmental reservoir is contained in a state such that the PCB content is gradually released with a time constant $\tau_2 \equiv 1/\lambda_2$. Thus, within the reference interval t to t + Δt, an amount

$$\lambda_2(1-\varepsilon)\alpha Q_s(t)\Delta t \tag{2-17}$$

enters the mobile pool.

Further, a fraction β of the yearly sales was used to manufacture long lived electrical components, assumed to have a useful life of γ_1 years, after which the components are scrapped. Thus, the contribution of this source to the general environmental pool is

$$\beta\, Q_s(t-\gamma_1)\Delta t \tag{2-18}$$

The electrical containers in which the PCB is enclosed will eventually decay, with a half life $\tau_1 = 1/\lambda_1$. The additional component entering the mobile reservoir will be

$$\lambda_1\beta\, Q_s(t-\gamma_1)\Delta t \tag{2-19}$$

Finally, the remainder $(1-\alpha-\beta)Q_s(t)$ was used in the construction of products assumed to have a useful life of γ_2 years, after which they are discarded, thus contributing a component to the general environmental pool:

$$(1-\alpha-\beta)\; Q_s(t-\gamma_2)\Delta t \tag{2-20}$$

If it is further assumed that these products have a lifetime $\tau_2 = 1/\lambda_2$ against decay, then the contribution to the mobile environmental pool will be

$$\lambda_2(1-\alpha-\beta)\; Q_s(t-\gamma_2)\Delta t \tag{2-21}$$

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On combining Equations (2-16), (2-17), (2-15) and (2-21), in the limit $\Delta t \to o$, the differential equation for $m_{ev}(t)$ becomes

$$\frac{dm_{ev}(t)}{dt} = \varepsilon\alpha Q_s(t) + \lambda_2(1-\varepsilon)\alpha Q_s(t) + \lambda_1\beta Q_s(t-\gamma_1)$$

$$\lambda_2(1-\alpha-\beta)Q_s(t-\gamma_2) \qquad (2\text{-}22)$$

$$= \left[\varepsilon\alpha + \lambda_2(1-\varepsilon)\alpha\right] Q_s(t) + \lambda_2(1-\alpha-\beta)Q_s(t-\gamma_2) + \lambda_1\beta Q_s(t-\gamma_1)$$

but, from Equation (2-3), $Q_s = 311t^{3.39} = \delta t^{3.39}$

If the parametric values given in Table 2.3.1-1 are substituted into Equation (2-22), the equation becomes

$$m_{ev}(t) = 24.32\int_o^t t^{3.39}\,dt + 6.53\int_o^t (t-4)^{3.39}\,dt + 1.93\int_o^t (t-20)^{3.39}\,dt$$

$$= \frac{24.32}{4.39}\,t^{4.39} + \frac{6.53}{4.39}\,(t-4)^{4.39} + \frac{1.93}{4.39}\,(t-20)^{4.39}$$

Thus,

$$m_{ev}(t) = 5.54t^{4.39} + 1.49(t-4)^{4.39} + 0.44(t-20)^{4.39} \qquad (2\text{-}23)$$

The results computed from Equation (2-23) are tabulated in Table 2.3.1-2

2.3.2 Effect of 1970 Ban on Mobile PCBs

It is now appropriate to discover the effect that the partial ban established in 1970 can be expected to have on the mobile PCB load, $m_{ev}(t)$.

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TABLE 2.3.1-1

Parameter Values for Equation (2-22) and Equation (2-24)

$\alpha = 0.17$	$\epsilon = 0.40$	$\lambda' = 0.1$
$\beta = 0.62$	$1-\epsilon = 0.60$	$\delta = 311$
$1-\alpha-\beta = 0.21$		$\delta' = 3.31 \times 10^7$

$\lambda_2 = 0.1$, $\tau_{2-1/2} = 6.9$ years

$\lambda_1 = 0.01$, $\tau_{1-1/2} = 69$ years

$\gamma_2 = 4$ years $\gamma_1 = 20$ years

The operative change occurs as a result of the substitution of Equation (2-6) for Equation (2-3) in the time interval after 1970. The resulting expression for $m_{ev}(t \geq 40)$ is given as (recalling that the ban also stopped sales for non-electrical applications):

$$m_{ev}(t > 40) = c\alpha\delta \int_0^{40} t^{3.39}dt + c\alpha'\delta' \int_0^{t-40} dt + \lambda_2(1-\varepsilon)\alpha\delta \int_0^{40} t^{3.39}dt$$
$$+ \beta\lambda_1\delta \int_0^{t} (t-\gamma_1)^{3.39}dt + (1-\alpha-\beta)\lambda_2\delta \int_0^{t\leq 44} (t-\gamma_2)dt \qquad (2\text{-}24)$$

which, on integration and evaluation of the coefficients, becomes, using the parametric values listed in Table 2.3.1-1,

$$m_{ev}(t \geq 45) = 7.59 \times 10^7 + (0.44)(t-20)^{4.39} + 1.32 \times 10^6 (t-40). \qquad (2\text{-}24^1)$$

Numerical values derived from Equation (2-24^1) are listed in column 4 of Table 2.3.2-1. Again, the effect of the voluntary partial ban of 1970-71 is apparent.

It will be useful in what follows to express the numerical relationship given by Equation (2-24^1) in the approximate empirical form

$$\left.\begin{aligned} m_{ev}(t \leq 40) &= 4.83t^{4.5} \\ m_{ev}(t > 40) &= 1.69 \times 10^6 t^{1.02} \end{aligned}\right\} \qquad (2\text{-}25)$$

2.4 Atmospheric Reservoir of PCBs, $m_a(t)$

Suppose that some fraction θ of the instantaneous addition to the mobile environmental material is vaporized. Then within the interval t to t + Δt

$$\left[\frac{dm_a(t)}{dt}\right]_a = \theta \frac{dm_{ev}(t)}{dt} \Delta t$$

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TABLE 2.3.2-1

Estimated Total Environmental PCB Load [$M_{ev}(t)$]
and Mobile Environmental PCB Load [$m_{ev}(t)$]

Date	t (years)	$m_{ev}(t)$ (1) (lbs)	$m_{ev}(t)$ corr (2) (lbs)	$M_{ev}(t)$ corr (3) (lbs)
1930	0	0	0	0
1935	5	6.49×10^3		1.42×10^4
1940	10	1.40×10^5		3.35×10^5
1945	15	8.62×10^5		2.32×10^6
1950	20	3.14×10^6		9.1×10^6
1955	25	8.54×10^6		2.62×10^7
1960	30	1.89×10^7		6.23×10^7
1965	35	3.86×10^7		1.31×10^8
1970	40	7.01×10^7	7.01×10^7	2.54×10^8
1975	45	1.19×10^8	8.31×10^7	3.76×10^8
1980	50	1.90×10^8	9.04×10^7	4.66×10^8
1990	60	4.30×10^8	1.07×10^8	8.41×10^8

Notes: (1) From Equation (2-23)
(2) From Equation (2-24[1])
(3) From Equation (2-15)

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Further, suppose that the material contained within the mobile pool is vaporized with a time constant $\tau_3 = 1/\lambda_3$, then the additional component of the atmospheric reservoir is given by

$$\left[\frac{dm_a(t)}{dt}\right]_b = \lambda_3 m_{ev}(t)$$

Finally, suppose that the lifetime, $\tau_4 = 1/\lambda_4$, of the atmospheric reservoir results in a decay of $m_a(t)$ given as

$$\left[\frac{dm_a(t)}{dt}\right]_c = -\lambda_4 m_a(t).$$

The total change in $m_a(t)$ with time is then given as

$$\frac{dm_a(t)}{dt} = \left[\frac{dm_a(t)}{dt}\right]_a + \left[\frac{dm_a(t)}{dt}\right]_b + \left[\frac{dm_a(t)}{dt}\right]_c \qquad (2\text{-}26)$$

which on substitution of the appropriate expressions yields the differential equation for $m_{ev}(t)$ as follows:

$$\frac{dm_a(t)}{dt} + \lambda_4 m_a(t) = 0\,\frac{dm_{ev}(t)}{dt} + \lambda_3 m_{ev}(t) \qquad (2\text{-}27)$$

for which the general solution is

$$m_a(t) = e^{-\lambda_4 t}\int_0^t \left[0\,\frac{dm_{ev}(t)}{dt} + \lambda_3 m_{ev}(t)\right] e^{\lambda_4 t}\,dt \qquad (2\text{-}28)$$

After substitution from Equation (2-25a) and integrating by parts, the interim result is

$$m_a(t) = \frac{4.83}{\lambda_4}\left\{\lambda_3 t^{3.5} - 4.5\left(\frac{\lambda_3}{\lambda_4} - 0\right)\left[t^{3.5} - \frac{3.5t^{2.5}}{\lambda_4}\right.\right.$$

$$\left.\left. + \frac{(3.5)(2.5)}{\lambda_4^2}\,t^{1.5} - \frac{(3.5)(2.5)(1.5)}{\lambda_4^3}\,e^{-\lambda_4 t}\int_0^t t^{0.5} e^{\lambda_4 t}\,dt\right]\right\} \qquad (2\text{-}29)$$

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It now becomes important to evaluate the parameters, λ_3, λ_4, and θ which appear in (2-29). First, it is noted that the cumulative total of material entering the environment from 1930 to some time t is given by the sum

$$\sum m_a(t) = \int \left[\theta \frac{dm_{ev}(t)}{dt} + \lambda_3 m_{ev}(t) \right] dt \qquad (2\text{-}30)$$

since the two terms in the integral are simply source terms. On substitution for $m_{ev}(t)$ from Equation (2-25) and carrying out the integration, Equation (2-30) becomes, after simplification,

$$\sum_{1930}^{t} m_a(t) = 4.83t^{4.5} \left[\theta + \frac{\lambda_3}{5.5} t \right] \quad \text{(lbs)} \qquad (2\text{-}31)$$

It is important at this point to indicate the essential difference between Equation (2-29) and (2-31). The latter, Equation (2-31), represents the cumulative PCB load to the atmosphere in the time from 1930 to the time $t > 1930$. On the other hand, Equation (2-29), which contains the time constant for decay of the atmospheric PCB load, represents the instantaneous PCB load in the atmosphere at time t.

To return to Equation (2-30). Nisbet and Sarofim[7] have estimated that the cumulative load of vaporized PCB in the period 1930 through 1970 was 3×10^4 tons or 6×10^7 lbs. If it is assumed that θ, the fraction of free PCB directly vaporized, is 0.1, then Equation (2-31) may be used to evaluate λ_3 as follows:

$$\sum_{1930}^{1970} m_a(t) = 6 \times 10^7 = 4.83(40)^{4.5} \left[0.1 + \frac{40\lambda_3}{5.5} \right]$$

$$\lambda_3 = 0.0918 \text{ yrs}^{-1}$$

$$\text{and} \quad (\tau_3)_{1/2} = 7.55 \text{ yrs.} \qquad (2\text{-}31')$$

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In view of the results displayed in Equation (2-31[1]) and with the additional assumptions that $\lambda_4 >> \lambda_3$, $\lambda_4 > 1$, Equation (2-29) may be approximated as

$$m_a(t) = \frac{4.83}{\lambda_4} t^{3.5} \left\{ \lambda_3 t + 4.5\theta \right\} \qquad (2\text{-}32)$$

By definition of $\sigma(t)$, the fallout,

$$\sigma(t)A = \lambda_4 m_a(t) = 4.83 t^{3.5} \left\{ \lambda_3 t + 4.5\theta \right\}$$

where $A = 8.66 + 10^{13}$ ft^2 as the area of continental United States. Solving for $\sigma(t)$,

$$\sigma(t) = \frac{4.83 t^{3.5}}{A} \left\{ \lambda_3 t + 4.5\theta \right\} \qquad (2\text{-}33)$$

where upon, in 1974, $\sigma(t) = 1.06 \times 10^{-8}$ lbs/ft^2/sec, (2-33) yields a value of

$$\sigma(t = 1974) = 1.3 \times 10^{-7} \text{ lbs/ft}^2\text{/yr.},$$

a result clearly not consistent with the known value. The obvious suggestion to account for this discrepency is that the Nisbet[7] value of the cumulative atmosphere load from 1930 through 1970 is incorrect. However, no conclusion as to the reason for this can be reached at present.

2.4.1 Time Dependence of $\sigma(t)$ and of B(t)

From Equation (2-33) and the known value of $\sigma(t)$ in 1974 (1.06×10^{-8} lbs/ft^2/yr), it is apparent that Equation (2-33) yields the correct value if the term $\lambda_3 t << 4.5\theta$, so that, it is appropriate to take, where $\theta = 0.1$

$$\sigma(t) = \sigma_c(t) t^{3.5} \text{ lbs/ft}^2\text{/yr} \qquad (2\text{-}34)$$

and, since fallout constitutes the predominant PCB input source to Lake Michigan (see Section 3), the forcing function B(t) will be taken to be of the form

$$B(t) = \alpha t^{3.5} \qquad (2\text{-}35)$$

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The coefficient α will be evaluated in terms of the specific application for which Equation (2-35) is the driving function.

3.0 DERIVATION OF PHYSICAL CONSTANTS FOR LAKE MICHIGAN

3.1 General Properties[8]

From various atlas and other sources, for Lake Michigan

$A = 2.24 \times 10^4$ mi^2 $= 6.24 \times 10^{11}$ ft^2 = area of lake.

$S = 1.2 \times 10^{14}$ lbs/yr [6×10^4 ft^3/sec in average flow through Straits of Mackinac]

$Q = 1.1 \times 10^{16}$ lbs = total water mass in lake.

$A' = 5 \times 10^4$ m^2 $= 1.29 \times 10^{12}$ ft^2 (average drainage area)

3.2 Proportioning Constants

In order to determine the most appropriate values for the proportionality constants, ρ^* and η, in the absence of a well-founded theoretical explanation of the physical processes which determine them, it is necessary to rely on in-situ measurements of concentration over wide regions of the target water body to establish reasonable statistical reliability. Actually, such a body of data does not exist for Lake Michigan at this time. On the other hand, such data do exist for Lake Ontario which should allow at least a reasonable estimate of the appropriate values for Lake Michigan.

3.2.1 Concentration Ratio of Biota to Water, η

Sampling of Lake Ontario, conducted in 1972 at several near-shore and mid-lake sites, indicated the following:[9]

a. PCB in fish (alewives, smelt, slimy sculpin) = $2.35 - 5.13 \times 10^6$ ppt
b. PCB in water (total conc. dissolved + particulate) = 55 ppt
c. Average PCB in sediments = 1.2×10^5 ppt
d. Average PCB in wet plankton = 7.2×10^6 ppt
e. PCB in the benthos = 4.7×10^5 ppt

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In view of these data, it appears that a realistic value for the constant η, considering the nature of the food chain, is

$$[\eta \sim 4 \times 10^4]$$

for Lake Ontario which, by inference, should also apply to Lake Michigan. It should be noted that n is taken as an average concentration ratio over all members of the biota; thus, there will be specific species showing considerable variation from the assumed value.

Since the basic physical processes that account for this partitioning of PCB-like materials should be independent of the actual concentration of PCBs in the aqueous phase (so long as the aqueous solution is less than saturated), it is reasonable to assume that η is independent of time.

3.2.2 Concentration Ratio of Sediment to Water, ρ

From a number of measurements of sediment levels within Lake Michigan (24 sites),[10] an average PCB concentration of 38.2 ppb was calculated; this is the presence of an average water concentration of 20 ppt. Since these specific points were taken from the southern part of the lake, where the contamination is known to be higher, an average value of ρ has been taken to be:

$$\rho = 2 \times 10^3$$

The deposition rate for the lake, D, is[11]

$$D = 5.7 \times 10^6 \text{ lbs/mi}^2\text{/yr}$$

3.3 Biota Mass, G, for Lake Michigan

A representative value for the biomass in Lake Michigan, recognizing the relatively limited data that are available on specific species and the absence of a detailed ecological pyramid, may be obtained from the estimates contained in Table 3.3-1.

In addition, the relatively polluted nature of the southernmost portion of the Lake results in large masses of benthic species, such as tubifex

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TABLE 3.3-1

Estimates of Biota Mass for Lake Michigan

Estimates for the Fish Mass[12]

a. Lake trout (from Michigan waters of the Lake) - 11.2×10^6 lb (1972)

b. Whitefish (in Northern Lake Michigan) - 55×10^6 lb (1972)

c. Chubs (those available to bottom trawls) - 15×10^6 lb (1973)
(note: decline in chubs from 139×10^6 lb in 1963-65)

d. Alewives (those available to bottom trawls + estimate of the midwater individuals) - 2×10^9 lb (1973)

e. Coho Salmon (estimate based on the number stocked) - 7.6×10^6 lb (1972)

Total - 2.1×10^9 lb (1972-73)

Estimates for the Plankton Biomass:

a. Assume 300 kg plankton/hectare of lake

b. Area of Lake = 22,400 mi^2 = 5.8×10^6 hectares

c. Plankton biomass = $(5.8 \times 10^6)(300 \text{ kg}) = 1.74 \times 10^{12}$ g = 3.8×10^9 lb

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worms. In view of this, it is assumed that the benthic biomass is of the order of 4×10^9 lbs.

Finally, in terms of the above, a representative value for the total biotic mass, G, appears to be of the order of 10^{10} lbs which, in view of its approximate value, is taken to have been constant over the time interval of interest.

3.4 Input Rate [B(t)] for the Period 1973-1974

The PCB inputs to Lake Michigan consist of three parts:

a. that due to fallout on the lake;

b. that due to fallout on the drainage area and subsequent extraction by ground waters; and

c. that due to point sources, industrial and sewage treatment plants.

3.4.1 Point Source Inputs

Data on PCB concentrations are available only for eight of the tributary streams in Michigan. In addition, historical data collections seldom extend back beyond 1970-1972. These data, for the St. Joseph, Kalamazoo, Grand, Muskegon, Marristee, Broadman, Elk and Portage Rivers[13] indicate that, during the recent period, the yearly load of PCBs from these rivers was about 1000 lb/yr. Using these limited data on stream concentration due to industrial and sewage treatment plants, the following estimates of yearly load can be made:[14]

Michigan	-	217.2 lb/yr (1974, STPs)
Wisconsin	-	1,150.0 lb/yr (1974-75, paper plant effluents)
Wisconsin	-	130.3 lb/yr (1974-75, STPs)
Wisconsin	-	20.1 lb/yr (1974, misc. industry)
Indiana	-	123.3 lb/yr (1972, STPs)
Illinois	-	3.1 lb/yr (1971, STPs)
		1,644.0 lb/yr = 1.6×10^3 lb/yr

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3.4.2 Fallout on Lake Michigan

A variety of fallout rate measurements have been reported[17] indicating rates as high as 0.5 lbs/mi^2/yr = 87 μg/m^2/yr in the heavily industrialized portion of Sweden[15] to the other extreme of 17.5 μg/m^2/yr observed in Iceland.[16] In view of the rather heavy concentration of industry in the Lake Michigan area, it will be assumed that the average fallout in the 1974 era was 50 μg/m^2/yr.

Thus, taking the area of the lake to be 5.8×10^{10} m^2, the annual fallout should be of the order of

$$B_{\text{fallout direct}} \sim 6.4 \times 10^3 \text{ lbs/yr in 1974.}$$

3.4.3 Fallout onto Drainage Basin

In order to compute the contribution of PCB input to the lake due to fallout on the drainage basin, the separate contributions from each of the adjourning states is computed in Table 3.4.3-1.

3.4.4 Total Input to Lake (1974)

From Table 3.4.3-1 and the data in Sections 3.4.1 and 3.4.2, the contributions to the PCB input are taken to be:

Point sources	1.6×10^3 lbs/yr	
Lake fallout	6.4×10^3 lbs/yr	
Basin fallout	5.4×10^3 lbs/yr	(where it is assumed that 50 percent of basin fallout actually enters the lake)[12]

$$B(1973\text{-}74) = 13.4 \times 10^3 \text{ lbs/yr}$$

From Equation (2-35),

$$B(t) = \alpha t^{3.5}$$

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TABLE 3.4.3-1

PCBs Inputs to Lake Michigan - 1974

a. For the Michigan portion of the drainage basin:[18]

PCB load = $(50\ \mu g/m^2/yr)(6.0 \times 10^{10}\ m^2) = 3 \times 10^{12}\ \mu g$ PCB/yr

$= 6.6 \times 10^3$ lb PCB/yr

b. For the Wisconsin portion of the drainage basin:[19]

PCB load = $(50\ \mu g/m^2/yr)(3.7 \times 10^{10}\ m^2) = 1.9 \times 10^{12}\ \mu g$ PCB/yr

$= 4.1 \times 10^3$ lb PCB/yr

c. For the Illinois portion of the drainage basin:[20]

PCB load = $(50\ \mu g/m^2/yr)(8.0 \times 10^{8}\ m^2) = 4.0 \times 10^{10}\ \mu g$ PCB/yr

$= 88.1$ lb PCB/yr

d. For the Indiana portion of the drainage basin:[21]

PCB load = $(50\ \mu g/m^2/yr)(1.85 \times 10^{8}\ m^2 = 9.3 \times 10^{9}\ \mu g$ PCB/yr

$= 20.4$ lb PCB/yr

e. Total annual fallout from all four sectors of the basin:

$= 1.08 \times 10^4$ lb PCB/yr

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which for the reference year, 1974, was estimated to be

$$13.4 \times 10^3 = \alpha (44)^{3.5}$$

$$\alpha = .0237$$

so that, in what follows,

$$B(t) = 0.0237t^{3.5} \qquad (3\text{-}1)$$

4.0 APPLICATION OF THE MASS BALANCE EQUATION TO LAKE MICHIGAN

4.1 Physical and Hydrologic Constants for Lake Michigan

The values used for the various physical and hydrologic constants for Lake Michigan are listed below:[23]

- A = surface area of the lake = 6.24×10^{11} ft^2
- S = outflow through Strait of Mackinac = 1.2×10^{14} lb/yr
- Q = water mass in lake = 1.1×10^{16} lbs
- D = sediment deposition rate = 0.204 lbs/ft^{2}yr
- η = biota/water concentration ratio = 4×10^4
- ρ = sediment/water concentration ratio = 2×10^3
- B (1974) = PCB input rate in 1974 = 1.34×10^4 lbs
- K = evaporation rate constant = 2.2×10^{14} lbs/yr
  [this assumption will be discussed below]

Then, from the data above, the various factors appearing in Equation (1-9') may be evaluated as follows:

$$AD\rho = 2.25 \times 10^{14} \text{ lbs/yr}$$

$$Q + G\eta = 1.14 \times 10^{16} \text{ (lbs)}, \quad (Q + G\eta)^{-1} = 8.77 \times 10^{-17} \text{ (lbs)}^{-1}$$

$$S + K + AD\rho = 5.7 \times 10^{14} \text{ lbs}$$

$$X = \frac{S + K + AD\rho}{Q + G\eta} \sim 0.05$$

$$Y = \frac{1}{Q + G\eta} = 8.77 \times 10^{-17}$$

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4.2 Integration of the Mass Balance Equation

In terms of the parameters for the lake and the assumed form for B(t) from Equation (3-1), the differential equation for C(t), Equation (1-9) becomes:

$$C(t_f) = 2.08 \times 10^{-18} e^{-0.05t_f} \int_0^{t_f} t^{3.5} e^{0.05t} dt \qquad (4\text{-}1)$$

where the PCB concentration is taken to be zero in 1930, i.e., at t = 0.

Equation (4-1) cannot be directly integrated in terms of simple algebraic functions so that recourse must be had to numerical integration to yield the results tabulated in Table 4.2-1.

For convenience in what follows, the relationship between $C_w(t_f)$ and t_f will be assumed to be of the form:

$$C_w(t_f) = bt^n$$

where b, and n are determined by a least squares fit to the data in Table 4.2-1. The results of this analysis may be summarized in the equation

$$C_w(t_f) = 4.56 \times 10^{-19} t_f^{4.416} \qquad (4\text{-}2)$$

From Equation (4-2), the change in $C_w(t)$ over a one-year period is found to be

$$\frac{dC_w(t)}{dt} = 2.01 \times 10^{-18} t^{3.416} \qquad (4\text{-}2^1)$$

Thus, for the reference year, 1974, the average water concentration was about 8×10^{-12} and the change in concentration during the reference year was 0.80×10^{-12}. From these data, it is possible to determine the material balance during 1974 as is shown below:

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Total input	1.34×10^4 lbs
Increase in solution	8.81×10^3 lbs
Increase in biota	0.32×10^3 lbs
Increase in sediment	1.8×10^3 lbs
Increase in outflow	0.96×10^3 lbs
Net loss due to evaporation	1.52×10^3 lbs

From Equation (1-6), it is now possible to estimate the evaporation rate constant K,

$$K = \frac{\Delta m_{evap}}{\bar{C}_w} = \frac{1.52 \times 10^3}{8 \times 10^{-12}} \sim 2 \times 10^{14} \text{ lbs/yr}$$

To discover the material balance over the entire period, 1930 through 1975, the total PCB input to the Lake is given by

$$Q_{input} = \int_0^{45} B(t)dt = 0.0237 \int_0^{45} t^{3.5}\, dt$$

$$= 1.49 \times 10^5 \text{ lbs} \qquad (4\text{-}3)$$

The average concentration $\bar{C}_w(t)$ over the reference period is

$$\overline{C_w(t)} = \frac{4.56 \times 10^{-19}}{45} \int_0^{45} t^{4.416} dt \qquad (4\text{-}4)$$

$$= 1.68 \times 10^{-12}$$

The cumulative loads in Lake Michigan in the various phases are summarized below:

Total input (1930-1975)	$= 1.49 \times 10^5$ lbs
Total in water	$= 1 \times 10^5$ lbs
Total in biota	$= 3.64 \times 10^3$ lbs
Total in sediments	$= 1.7 \times 10^4$ lbs
Total in outflow	$= 9.07 \times 10^3$ lbs
Net loss due to evaporation	$= 1.93 \times 10^4$ lbs

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TABLE 4.2-1

Concentration of PCB in Solution in Lake Michigan*

Date	t_f	$C_w(t_f)$	$C_w(t_f)$ (ppt)
1930	0	0	0
1935	5	4.94×10^{-16}	4.94×10^{-14}
1940	10	1.34×10^{-14}	1.34×10^{-2}
1950	20	2.79×10^{-13}	0.28
1960	30	1.60×10^{-12}	1.60
1965	35	2.92×10^{-12}	2.92
1970	40	5.35×10^{-12}	5.35
1975	45	9.10×10^{-12}	9.10

*Measurements in 1970 indicate a range of aqueous concentration of 1 to 7.5 ppt[13]

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From the net loss of PCB due to evaporation from the above data, and the defining equation for the evaporation losses, Equation (1-6), the evaporation rate constant K may be evaluated,

$$K = \frac{\Delta m_{evap}}{\bar{C}_w(t)\Delta t} = \frac{1.93 \times 10^{4}}{1.68 \times 10^{-12} \times 45} = 2.56 \times 10^{14} \text{ lbs/yr} \qquad (4\text{-}5)$$

The several values of K, from Equation (4-5) and the earlier value determined from the 1974 situation, are averaged to yield a useful value

$$K = 2.2 \times 10^{14} \text{ lbs/yr} \qquad (4\text{-}6)$$

4.3 Temporal Variation of Concentration of PCB in the Various Phases of the Lake

It is now possible to combine the relationship expressed by Equation (4-2) with the definition of the biotic concentration factor η from Equation (1-2), to determine the variation of biotic concentration with time. The data enumerated in Table 4.3-1 indicate the trends. When it is noted that the concentration data in Table 4.3-1 are given in parts-per-trillion, it is clear that the average biota concentration neared the one part-per-million level on as early as 1965. It is also evident, because of the considerable spread in specific biotic concentration factors for specific species, that the higher predictors could easily have exceeded the one ppm level as early as 1960.

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TABLE 4.3-1

Temporal Variation of Biotic Concentration

Date	C_w (ppt)	C_{biota} (ppt)
1930	0	0
1935	4.9×10^{-4}	1.97
1940	1.34×10^{-2}	5.36×10^{2}
1945	7.12×10^{-2}	2.84×10^{3}
1950	0.28	1.12×10^{4}
1955	0.68	2.72×10^{4}
1960	1.60	6.4×10^{4}
1965	2.92	1.17×10^{5}
1970	5.35	2.14×10^{5}
1975	9.10	3.64×10^{5}

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4.4 Physical Interpretation of K, the Mass Evaporation Constant

4.4.1 Kinetic Theory

Experimental data[24] on the evaporation rate of Aroclor 1254 indicates that, at 100°C (373°K), the evaporation rate is 1.47×10^{-8} gm/cm²/sec and the vapor pressure is 5×10^{-2} mm Hg. From elementary kinetic theory of gases,[25] the relationship between evaporation rate and vapor pressure is given

$$m(gm/cm^2/sec) = \delta\left[\frac{m}{2\pi RT}\right]^{1/2} P \qquad (4\text{-}7)$$

where δ = the measure of the probability that a collision with the surface does not result in the molecule sticking to the surface

R = the gas constant per mole [8.31×10^7 erg $(°K)^{-1}$]
T = the absolute temperature [°K]
m = the molecular weight [gms]
P = the vapor pressure [dynes/cm²]

From Equation (4-7) and the known evaporation rate,[24] the numerical value of δ may be computed as follows:

$$1.47 \times 10^{-8} = \delta\left[\frac{325}{2\pi \times 8.31 \times 10^7 \times 373}\right]^{1/2} \frac{5 \times 10^{-2}}{760} \times 10^6$$

$$\text{or} \qquad \delta = 5.47 \times 10^{-6} \qquad (4\text{-}8)$$

If it is assumed that δ is not temperature dependent at temperatures considerably removed from the normal boiling temperature, and that Equation (4-7) may be applied to a solution as well as to the pure liquid, then at ambient temperature (298°K) where the vapor pressure of Aroclor 1254 is 7.7×10^{-5} mm Hg,[24]

$$m(gm/cm^2/sec) = 5.47 \times 10^{-6}\left[\frac{325}{2\pi \times 8.3 \times 10^7 \times 298}\right]^{1/2} \frac{7.7 \times 11^{-5}}{760} \times 10^6$$

$$\text{or} \qquad m = 2.53 \times 10^{-11} \text{ gm/sec/cm}^2$$

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Now the area of the lake is 5.8×10^{14} cm^2, hence

$$m(\text{lbs/year}) = 2.08 \times 10^{14} \text{ (lbs/yr)} \qquad (4\text{-}9)$$

The value of m from Equation (4-9) is in excellent agreement with the value of K empirically determined to be 2.2×10^{14} lbs/yr.

4.4.2 Application of the Theory of MacKay and Wolkoff[26]

Following MacKay and Wolkoff,[26] the rate of material loss for a slightly soluble solute from a water-air interface is given, for a system wherein the solute concentration is less than the saturation concentration, by:

$$\frac{dC_i}{dt} = -\frac{EP_{is}M_i}{G'M_w P_w C_{is}} C_i \qquad (4\text{-}10)$$

where:
- A = area of the lake surface (6.24×10^{11} ft^2)
- E = mass evaporation rate of water (1.38×10^{12} lb/yr)[11]
- P_{is} = equilibrium vapor pressure of pure solute (7.7×10^{-5} mm Hg)[27]
- M_i = molecular weight of solute (325-Aroclor 1254)
- G' = mass of water from which evaporation occurs
- M_w = molecular weight of water (18)
- C_{is} = saturation concentration of solute (6×10^{-8})[27]
- P_w = equilibrium vapor pressure water (23.7 mm Hg)
- C_i = concentration of solute in the evaporation layer
- ρ = density of water (62.5 lbs/ft^3)

Equation (4-10) must be modified for the present situation to take into account the effect of fallout on the solute concentration. Thus, for the case in point,

$$\frac{dC_i}{dt} = \frac{\sigma(t)A}{G'} - \frac{EP_{is}M_i}{G'M_w P_w C_{is}} C_i \qquad (4\text{-}11)$$

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The expression $\sigma(t)$ which occurs in Equation (4-11) is taken to be of the form [from Equation (2-34)]

$$\sigma(t) = 1.67 \times 10^{-14} t^{3.5} \tag{4-12}$$

Further substitution of $G' = A\rho\xi$, where ξ is the thickness of the layer from which evaporation is occuring, and $E = A\rho l'$, where l is the evaporation rate in ft/year, reduces Equation (4-12) to the form

$$\frac{dC_i}{dt} = \frac{1.67 \times 10^{-14} t^{3.5}}{\xi\rho} - \frac{lP_{is}M_i}{\xi M_w P_w C_{is}} Ci \tag{4-12'}$$

which is now applicable to a unit area of the lake.

The solution of Equation (4-12') is complicated by the fact that ζ, the layer thickness, is unknown. To obtain some idea of the magnitude of ξ, it is reasonable to assume that

$$C_i(t) = \gamma C_w(t) \tag{4-13}$$

where γ may be a function of time. Substitution of Equation (4-13) and the appropriate numerical values with Equation (4-12) and evaluating for $t = 44$ years (1974), yields [after using Equation (4-2) for $C_w(t)$]

$$8.22 \times 10^{-13} \gamma + 2.66 \times 10^{-10} \frac{\gamma}{\xi} = \frac{1.51 \times 10^{-10}}{\zeta} \tag{4-14}$$

Now, $\frac{K}{A} = \frac{lP_{is}M_i}{\xi M_w P_w C_{is}} \gamma$ from the definition of K. Hence, from this last relation, evaluated at $t = 44$ years,

$$\frac{\gamma}{\xi} = 10.92 \tag{4-15}$$

Substitution of (4-15) into (4-14) yields

$$\gamma = 0.57$$
$$\xi = 0.052 \text{ ft}^{(28)} \tag{4-16}$$

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It is apparent, from Equations (4-16) and (4-13), that this analysis suggests that the average concentration in the layer is less than that in the bulk water, i.e., $\gamma < 1$. The reason for this apparent anomaly can be seen by recognizing that Equation (4-12) is in the form

$$\frac{dc}{dt} = \frac{\sigma(t)}{\xi P} - \lambda_i C_i \qquad (4\text{-}17)$$

where $\lambda_i \equiv \frac{lP_{is} M_i}{\xi M_w P_w C_{is}} = 617 \text{ yrs}^{-1}$

is the effective decay constant for the surface layer concentration. In terms of the half-life

$$(\tau_i)_{1/2} \sim 10 \text{ hours} \qquad (4\text{-}17^1)$$

Equation (4-17) may be integrated from a time t to $t + 1/\lambda$ to yield, where the interval is sufficiently short that $\sigma(t)$ may be assumed to be constant;

$$C_i = 0.37\, C_{io} + 3.34 \times 10^{-12} \qquad (4\text{-}18)$$

If the assumed relationship between C_i and C_w, given by Equation (4-13) is introduced as (C_{io} = PCBs concentration at time t)

$$C_o = \gamma C_{io}$$

$$C_i = \gamma(C_w + \Delta C_w) \sim \gamma C_w$$

then

$$\gamma(1 - 0.37) = \frac{3.34 \times 10^{-12}}{C_w}$$

$$\gamma = 0.74 \qquad (4\text{-}19)$$

This shows good agreement with the results expressed in Equation (4-16).

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5.0 RESULTS AND CONCLUSIONS

5.1 Results

Even though the model used is only first-order, it is apparently able to describe the relative significance of the natural processes which control the distribution of PCBs. The strong focus on fallout as the primary input source of PCBs to Lake Michigan suggests the need for further study of the nature of the processes by which PCBs become airborne and thus become part of the available atmospheric reservoir.

The attempt to model the atmospheric reservoir of PCBs, discussed in Section 2, yields results that indicate significantly greater cumulative atmospheric loads than the preliminary estimate, made by Nisbet and Sarofim,[7] of a cumulative atmospheric reservoir of 3×10^4 tons up to 1970. The estimate of Nisbet and Sarofim leads to a half-life, from the model, for PCBs in the atmospheric reservoir on the order of eight years. This value is considerably in excess of the reported lifetime measurements, on the order of 20 to 40 days, for atmospheric PCBs.[29] However, the observation that significant levels of PCBs are found in present snowfalls and in packed snow in Antarctica[30] suggests that the applicable half-life may indeed be considerably longer than 20 to 40 days.

It is suggested that further refinement of the environmental distribution model presented in Section 2 will lead to a resolution of this apparent discrepancy. This refinement will focus attention on the nature of the physical processes involved in atmospheric transport of PCBs and may suggest methods of reducing PCB fallout in the future.

The observation that evaporation and/or co-distillation seems to be a significant process by which PCBs are returned to the atmosphere is of importance. It should be noted that the magnitude of the evaporation rate constant necessary to achieve mass balance in Lake Michigan is in excellent agreement with that computed from the simple kinetic theory of gases and also with that computed from the theory of co-distillation discussed by MacKay and Wolkoff.[26]

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The observation that the PCB input to Lake Michigan from point sources seems to be a rather small part of the total input suggests that reduction of point source PCB effluents may only slowly correct the present problem.

5.2 Conclusions

The first-order mass balance model described herein seems useful in describing the historical situation as it explicitly addresses the question "How did we get here?". The model requires refinement before it can be used to allow a reasonable estimate of future conditions. Significantly more detailed data are required as to the temporal variation of inputs and concentrations as well as on the interval transport processes by which localized concentrations are smoothed and distributed over the whole body. While the present model seems to deal very well with the situation that obtains during an interval of rising aqueous concentrations, there seems to be little experimental or theoretical guidance as to what will happen if, in the future, aqueous concentrations begin to fall. It is not known whether the biota and the sediments will act as reservoirs to return their PCB loads to the system. The processes, if any exist, which will eventually remove or inactivate the PCBs already in the lithosphere are not known.

The application of this model to the situation in Lake Michigan seems successful. It will be of interest to apply it to regions which are more complex or of larger scale.

5.3 Discussion of Results

With regard to Lake Michigan, the mass balance indicates that this fresh water system (water, sediment, biota) serves as a significant sink for PCBs; this must also apply to many other fresh water systems. In the case of toxic metals, the oceans are generally recognized as an important ultimate sink, but this may not be the case for PCBs.

The theory developed by MacKay and Wolkoff,[26] as applied to Lake Michigan conditions, yields a lifetime against (until) evaporation of about

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ten hours. For seawater, this lifetime is greatly reduced by lower solubility of PCBs and higher evaporation rate, so that the calculated lifetime of PCBs in seawater against evaporation may be as low as ten minutes.

Although attachment to organic and living material may well be a factor, the above result indicates that PCBs tend to evaporate from salt water much more quickly than from fresh water. Then, on this basis, the terrestrial systems, such as fresh water lakes, forests, etc., must be regarded as partial sinks for PCBs in fallout; the PCBs lost from these systems reenter the atmosphere via direct evaporation or transport by rivers to salt water from which further evaporation occurs. New PCBs are added to the atmospheric load by direct evaporation, through inadequate incineration processes, or via water from runoff, industrial discharges, landfill leachate, etc.

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6.0 GLOSSARY OF SYMBOLS USED

A	Surface area of reference body of water (ft^2)
$B(t)$	PCB injection rate with reference body of water (lbs/yr)
$C_w(t)$	Aqueous PCB concentration
D	Sediment rate in reference body of water ($lb/ft^2/yr$)
G	Mass of biota in reference body of water (lbs)
K	PCB evaporation rate constant (lbs/yr)
$M_{ev}(t)$	Cumulative environmental PCB load (lbs)
$m_{ev}(t)$	Cumulative free environmental PCB load (lbs)
$m_a(t)$	Instantaneous atmospheric reservoir of PCBs (lbs)
Q	Mass of water in reference body of water (lbs)
$Q_{cap}(t)$	Cumulative PCB sales for capacitor application (lbs)
$Q_{electrical}(t)$	Cumulative PCB sales for electrical application (lbs)
$Q_{prod}(t)$	Cumulative PCB sales for production application (lbs)
$Q_{sales}(t)$	Cumulative PCB sales for all applications (lbs)
$Q_{trans}(t)$	Cumulative PCB sales for transformer application (lbs)
S	Water outflow rate from reference body of water (lbs/yr)
t	Time (yrs), (t = 0 in 1930)
α	Fraction of PCB sales directly lost to the environment
β	Fraction of PCB sales devoted to electrical applications
γ_1	Average in-service life of electrical components (yrs)
γ_2	Average in-service life of non-electrical products (yrs)
ε	Fraction of production waste initially free
θ	Fraction of initially free PCBs that are vaporized

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λ_1	Decay constant for discarded PCB-containing electrical components (yr^{-1})
λ_2	Decay constant for discarded PCB-containing non-electrical products (yr^{-1})
λ_3	Decay constant for vaporization of free PCBs (yr^{-1})
λ_4	Decay constant for fallout of atmospheric PCBs (yr^{-1})
η	Ratio of biota PCB concentration to aqueous PCB concentration
ρ	Ratio of sediment PCB concentration to aqueous PCB concentration
$\sigma(t)$	Fallout rate per unit area ($lbs/ft^2/yr$)
τ_1	Half-life of containment of discarded PCB-containing electrical components (yr)
τ_2	Half-life of containment of discarded PCB-containing non-electrical components (yr)
τ_3	Half-life of free PCBs for vaporization (yr)
τ_4	Half-life of atmospheric PCBs against evaporation (yr)

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MONS 053003

APPENDIX E

BACKGROUND DATA USED TO CONSTRUCT
THE MODEL FOR PCBs IN LAKE MICHIGAN

Table E-1

Concentration of PCBs in Sediments
Along the Southwestern Shore of Lake Michigan (1970-1971)[1]

Sample Locations	PCBs (ppb)	
Along SW shore of lake;	13.09 A	15.24 B
sampling 1-3 mi. off-shore*	6.73 A	16.09 ?
(see Figure E-1).	11.81 ?	12.69 ?
	26.07 A	23.53 A
	87.89 A	17.53 A
	130.27 ?	36.7 ?
	26.61 B	58.81 A
	64.32 A	41.06 A
	3.72 A	132.61 A
	3.87 A	80.63 ?
	35.8 A	29.29 A
	8.31 A	13.34 A
	Total = 896.01	
	Ave. |PCB| = 37.3	

NOTE: Estimated location of sampling sites with respect to thermocline: A - above thermocline
B - below thermocline
? - questionable

* Sampling sites are located in an area with several known STP discharges. Data were not available on PCB concentrations in these STP effluents; however, judging from PCB data for other area STPs, it is probable that these plants discharge PCBs, thereby producing higher concentrations in the adjacent sediments.

MONS 053004

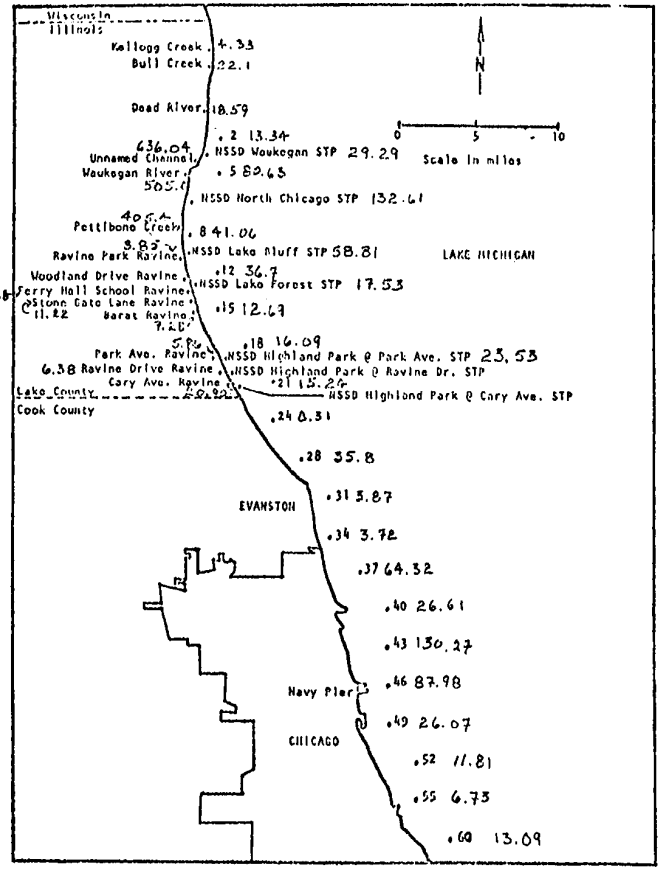

FIGURE E-1. LOCATIONS OF SEDIMENT SAMPLING STATIONS

PCBs in sediments of Lake Michigan & Tributary streams, ravines sediments.

MONS 053005

Table E-2

Concentration of PCBs in Michigan Streams Tributary to Lake Michigan[2,3,4]

Stream	PCB (ppb; mean 1971-72)	Stream Discharge (1974) (CFS)	(MGD)	PCBs lb/day	lb/yr
St. Joseph	0.013	4,204	2,716	0.29	105.9
Kalamazoo	0.065	2,162	1,397	0.75	275.1
Grand	0.041	5,814	3,756	1.28	466.5
Muskegon	0.010	2,489	1,608	0.13	47.5
Manistee	0.014	2,047	1,322	0.15	54.8
Boardman	0.017	187	121	0.02	7.3
Elk	0.012	575	371	0.04	14.6
Portage	0.47*	18	12	0.045	16.5
TOTAL		17,478	11,291		988.2

*One-time measurement taken in 1972.

MONS 053006

Table E-3

PCBs Entering Lake Michigan From Known Industrial and STP Discharges*

State	PCB Load (lb/yr)	Source
Michigan	217.2	STPs
Wisconsin	1170.1	Industries
Wisconsin	130.3	STPs
Indiana	122.3	STPs
Illinois	3.1	STPs
Total	1643	

*See Tables E-4 - E-9 for tabulations of the individual waste discharges.

MONS 053007

TABLE E-4

Concentration of PCBs in Reported Michigan STP Effluents Tributary to Lake Michigan[1,2,3,4]

STP Location	Design Flow (MGD, 1974)	[PCB] (ppb, 1971-72)	PCB Load (lb/day)
Albion	4.0	0.44	0.015
Battle Creek	22.0	0.39	0.017
Benton Harbon, St. Joseph Plant	13.0	0.65	0.070
Menominee	1.2	0.35	0.004
Muskegon	10.0	0.28	0.023
Niles	10.0	0.68	0.056
Portage	3.6	1.9	0.057
East Lansing	8.5	0.5	0.035
Escanaba	2.2	0.29	0.005
Holland	4.5	0.6	0.022
Jackson	20.0	<0.1	
Kalamazoo	34.0	0.66	0.186
Lansing	34.0	0.18	0.051
Total	147.0*		0.595*

PCB Load = 0.595 lb/day = 217.2 lb/yr.

* Total does not include flows with [PCB] <0.1 ppb.

MONS 053008

TABLE E-5

Concentration of PCBs in Reported Wisconsin Paper Plant Effluents Discharging to Green Bay (1974-75) (5)

Plant	Flow (mgd)	[PCB] (ppb)	PCB Load (lb/day)
Badger Paper Mills	4.78	<.1	-
Scott Paper			
Marinette	5.91	<.1	-
Oconto Falls	11.03	<.1	-
Shawano Paper	2.43	<.1	-
John Strange Paper	1.11	4.00	0.037
Bergstrom Paper	5.22	28.40	1.26
Kimberly Clark	4.30	0.28	0.010
Thilmany Paper	25.1	<.1	-
Fort Howard Paper			
Mill Effluent	7.3	2.60	0.158
Deinking	11.04	6.40	0.586
Deinking & Mill Effluent	18.1	7.07	1.06
American Can			
Sulfite Sewer	2.23	0.1	0.002
Paper Mill Lagoon	10.35	0.14	0.012
Chamin Paper	16.3	0.14	0.019
Green Bay Packaging	1.77	0.45	0.006
Total*	77.65		3.15

PCB load = 3.15 lb/day - 1,150 lb/yr.

* Total does not include flows with [PCB] <0.1 ppb.

MONS 053009

TABLE E-6

Concentration of PCBs in Reported Wisconsin Miscellaneous Industrial Effluents Discharged to Lake Michigan[5]

Plant	Flow (mgd)	[PCB] (ppb)	PCB Load (lb/day)
Motor Casting Co.	0.22	<0.1	
Grey Iron Foundry, Inc.	0.339	<0.2	
Howmett, Corp. - Crucible Steel	0.796	<0.1	
Maynard Steel Casting Corp.	0.133	<0.1	
Milwaukee Solvay Coke Co.	4.3	<0.1	
Briggs & Stratton	1.523	<0.2	
Wahr Steel Co.	0.228	<0.1	
EST Co.	0.069	2.95	0.001
Milwaukee Die Casting Co.	0.012*	32.2	0.003
Meta-Mold Daton Malleable Inc.	0.033*	170.3	0.047
Babcock & Wilcox Co. Tubular Products Div.	0.6	0.9	0.004
Total**	0.714		0.055

PCB load - 0.055 lb/day = 20.1 lb/yr.

* Average of two readings.

** Total does not include flows with [PCB]<0.1 ppb.

MONS 053010

TABLE E-7

Concentration of PCBs in Reported Wisconsin STP Effluents Discharged to Green Bay (1974-75) (5)

STP Location	Flow (mgd)	[PCB] (ppb)	PCB Load (lb/day)
Marinette	2.5	<0.1	
Portage	0.736	5.0	0.031
Oshkosh	8.49	0.1	0.007
Neenak-Menash	12.75	0.16	0.017
Appleton	11.05	0.12	0.011
Kaukauna	1.25	<0.1	
DePere	23.45	0.5	0.01
Green Bay	30.64	<0.1	
Kewaunee	0.315	0.18	0.001
Two Rivers	2.28	0.2	0.004
Manitowoc	9.3	<0.1	
Sheboygan	11.04	1.1	0.11
Port Washington	1.59	0.2	0.003
Milwaukee (South Shore)	66.7	0.29	0.160
Milwaukee (S. Milwaukee)	2.42	0.12	0.003
Racine	16.92	<0.1	
Kenosha	18.88	<0.1	
Total	119.8*		0.357*

PCB load = 0.357 lb/day = 130.3 lb/yr.

* Total does not include flows with [PCB]<0.1 ppb.

MONS 053011

TABLE E-8

Concentration of PCBs in Reported Indiana STP Effluents Tributary to Lake Michigan (6)

STP Location	Flow (mgd)	[PCB] (ppb)	PCB Load (lb/day)
Michigan City	12.2	1.32	0.134
Valparaiso	4.0	0.24	0.008
Hobart	2.9	0.23	0.006
Hammond	42.6	<0.1	
East Chicago	18.7	0.1	0.016
Chestertown	1.6	<0.1	
Gary	50.5	0.38	0.159
South Bend	35.8	<0.1	
Mishawaka	10.39	0.13	0.011
Elkhart	17.5	<0.1	
Goshen	4.8	<0.1	
Nappanee	0.9	<0.1	
Kendallville	1.2	<0.1	
La Grange	0.185	<0.1	
Ligonier	0.434	<0.1	
Angola	0.784	0.17	0.001
Syracuse	0.305	0.13	0.0003
Total*	99.8		0.335

PCB load = 0.335 lb/day = 122.3 lb/yr.

* Total does not include flows with [PCB] <0.1 ppb.

MONS 053012

TABLE E-9

Concentration of PCBs in Reported Illinois STP Effluents Discharging to Lake Michigan[1]

STP Location	Flow (mdg)*	[PCB] (ppb)**	PCB Load (lb/day)
N.S.S.D., Waukegan	0.002	2.635	.00004
N.S.S.D., North Chicago Plant	1.2	0.831	.0083
Total	1.202		0.00834

PCB Load = 8.34×10^{-3} lb/day = 3.04 lb/yr.

* Data for 1975

** Data for 1971

MONS 053013

TABLE E-10

Lake Michigan Basin Hydrology[7,8,9,10,11]

Total mean river discharge (1974) of the 4 states (Michigan, Illinois, Wisconsin, and Indiana) into Lake Michigan = 34,508 cfs

$= 1.1 \times 10^{12}$ cf/yr

Total flow of water in the basin = 9.4 billion gpd

Flow diverted from Lake to Chicago = 2 billion gpd

Flow diverted through Straits of Mackinac = 67,000 cfs

Other withdrawl's from the Lake = 11.7 mgd

Volume of STP effluents entering Lake:

from Illinois = 27.6 mgd

from Indiana = 110.5 mgd

from Michigan = 161.6 mgd

from Wisconsin = 183.4 mgd

MONS 053014

TABLE E-11

Estimates of Fish Biomass in Lake Michigan (1972-73) [12]

Michigan Waters of Lake Michigan	- 11.2×10^6 lb. of lake trout (age group II & older); 1972
Northern Lake Michigan	- 55×10^6 lb. of whitefish (age groups I-VI); 1972
From bottom trawls of the Lake	- 220×10^6 lb. of alewife (age groups I & over); 1973
	- 15×10^6 lb. of chubs (age groups I & over); 1973
Total (1972-73)	- 3×10^8 lb.

If midwater alewives are included, the total could be in the range of 2.3×10^9 lb.

MONS 053015

Background Calculations Used to Construct the Model for PCBs in Lake Michigan

The concentration and total weight of PCBs in Lake Michigan at the present was calculated on the basis of PCB input to the lake from the following sources: 1) atmospheric fallout directly on the lake, 2) atmospheric fallout over the drainage basin of the lake, and 3) documented point source discharges from tributary industries and sewage treatment plants (STPs). The derived concentration in the water of 0.078 ppb PCB (or 8.4×10^5 lb.) represents the expected maximum amount of the chemical in the water, assuming a constant annual input PCBs over the past 40 years, and no loss of PCB from the lake.

A. Estimation of PCBs in the Lake Water Phase.

1. PCB load from atmospheric fallout directly on the lake surface:

   area of lake = 22,400 mi^2 = 5.8×10^{10} m^2 (13)

   Assume that the atmospheric fallout of PCBs has a constant annual rate of 50 $mg/m^2/yr.$, that PCBs are evenly distributed across the lake surface, and that the total accumulation over the past 40 years represents the present load;

   then the annual PCB fallout on the lake = $(50\ mg/m^2/yr)(5.8 \times 10^{10}\ m^2)$

   $= 2.9 \times 10^{12}$ $\mu g/yr.$

   $= 6.4 \times 10^3$ lb/yr of PCB

   The total fallout on the lake after 40 yrs = 2.6×10^5 lb. of PCB.

2. PCB load from atmospheric fallout on the lake drainage basin:

   Assume that fallout (at a constant annual rate of 50 μg PCB/m^2/yr) over the basin contributes the majority of the PCBs to the lake via runoff, and that all of the PCBs falling on the drainage basin eventually enter the lake,

   then the annual PCB load = $(50\ \mu g/m^2/yr)$ (area of drainage basin)

   For the Michigan portion of the drainage basin -(7)

   PCB load = $(50\ \mu g/m^2/yr)(6.0 \times 10^{10}\ m^2) = 3 \times 10^{12}$ μg PCB/yr

   $= 6.6 \times 10^3$ lb PCB/yr

MONS 053016

For the Wisconsin portion of the drainage basin -[8]

PCB load = $(50\ \mu g/m^2/yr)(3.7 \times 10^{10}\ m^2) = 1.9 \times 10^{12}\ \mu g$ PCB/yr
$= 4.1 \times 10^3$ lb PCB/yr

For the Illinois portion of the drainage basin -[9]

PCB load = $(50\ \mu g/m^2/yr)(8 \times 10^8\ m^2) = 4 \times 10^{10}\ \mu g$ PCB/yr
$= 88.1$ lb PCB/yr

For the Indiana portion of the drainage basin -[10]

PCB load = $(50\ \mu g/m^2/yr)(1.85 \times 10^8\ m^2) = 9.3 \times 10^9\ \mu g$ PCB/yr
$= 20.4$ lb PCB/yr

Total annual PCB fallout from all four sectors of the basin = 1.08×10^4 lb/yr and total fallout on the basin after 40 yrs = $(1.08 \times 10^4\ lb/yr)(40) = 4.3 \times 10^5$ lb PCB.

3. Total annual PCB load in the lake due to fallout = PCB load from drainage basin + PCB load from lake surface
$= 1.08 \times 10^4$ lb/yr + 0.64×10^4 lb/yr
$= 1.7 \times 10^4$ lb PCB/yr

4. Total fallout load of PCB after 40 years = $(1.7 \times 10^4\ lb/yr)(40\ yrs) = 6.9 \times 10^5$ lb PCB

5. PCB load entering the lake via tributary stream discharges:

Assume that the concentration of PCBs in the streams has remained constant over the past 40 years, with an annual PCB load equivalent to that in the most recently recorded data.

Data on PCB concentrations are available only for eight tributary streams from the state of Michigan (see Table 2). PCB measurements along the St. Joseph, Kalamazoo, Grand, Muskegon, Manistee, Boardman, Elk, and Portage Rivers indicate a total of 988.2 lb PCB/yr.[2,3,4]

MONS 053017

6. PCB load entering the lake from reported industrial and STP discharges:

Assume that the concentration of PCBs in the industrial and STP effluents has remained constant over the past 40 years, with an annual PCB load equivalent to that in the most recently recorded data, and that all the PCBs in the discharges eventually enter the lake.

The annual PCB load from the four tributary states is as follows: (see Tables 4-9):[2,3,4]

Michigan - 217.2 lb PCB/yr (from STPs)
Wisconsin - 1150.0 lb PCB/yr (from paper plant effluents)
- 130.0 lb PCB/yr (from STPs)
- 20.1 lb PCB/yr (from misc. industry)
Indiana - 123.3 lb PCB/yr (from STPs)
Indiana - 3.1 lb PCB/yr (from STPs)
TOTAL - 1644.0 lb PCB/yr = 1.6×10^3 lb/yr

7. The total PCB load in the water phase from all the above sources (i.e., fallout, industry, STPs, Michigan streams) = 1.98×10^4 lb/yr. = 7.9×10^5 lb PCB after 40 years of constant accumulation at this annual rate.

8. Concentration of PCBs in the lake water phase:

Calculation based on the lake water volume = 4.91×10^{15} l.

Annual concentration of PCBs =

$$\frac{(1.98 \times 10^4 \text{ lb PCB/yr})(454 \times 10^6 \text{ µg/lg})}{4.9 \times 10^{15} \text{ l}} = 0.002 \text{ ppb/yr}$$

Total maximum concentration of PCBs at present (after 40 years of constant accumulation) =

$$\frac{(7.9 \times 10^5 \text{ lb PCB})(454 \times 10^6 \text{ µg/lb})}{4.91 \times 10^{15} \text{ l}} = 0.073 \text{ ppb PCB}$$

MONS 053018

9. The above calculations estimate PCB fallout over the drainage basin based on the size of the drainage areas as computed from USGS stream flow data, and totaling 9.8×10^{10} m^2. These data were obtained from flow gaging stations, which were not all located at the mouths of the tributary streams; therefore, the calculated size of the drainage basin may be underestimated.

As an alternative to the above, the same calculations were performed, but using a value of 1.76×10^{11} m^2 for the area of the drainage basin (this area was estimated by the Lake Michigan Federation.[13]

Then, the annual PCB fallout over the basin =

$$\frac{(50\ \mu g\ PCB/m^2/yr)(1.76 \times 10^{11}\ m^2)}{454 \times 10^6}$$

$= 1.9 \times 10^4$ lb PCB/yr.

After 40 years of constant accumulation at this rate, PCB load =

7.6×10^5 lb PCB (from fallout)

For this larger basin, the total PCBs in the water phase (i.e. fallout + industrial & STP discharges)

$= 1.9 \times 10^4$ lb/yr + 0.16×10^4 lb/yr

$= 2.1 \times 10^4$ lb/yr of PCB

After 40 years of constant accumulation at this rate, the PCB load would be 8.4×10^5 lb.

The PCB concentration in the water phase is:

on an annual basis = $\frac{(2.1 \times 10^4)(454 \times 10^6)}{4.91 \times 10^{15}\ l} = 0.002$ ppb

After 40 years of constant accumulation at this rate =

$$\frac{(8.4 \times 10^5)(454 \times 10^6)}{4.91 \times 10^{15}\ l} = 0.078 \text{ ppb}$$

MONS 053019

B. Estimates of PCB Transport in Lake Ontario, with Application to Lake Michigan.

Sufficient data were not available for Lake Michigan to determine the relationship of PCB concentrations between the water, sediment, and biotic phases. Adequate data were available to determine this relationship for Lake Ontario, and due to the similarities between the two lakes, the calculations were then used to estimate the present situation in Lake Michigan.

1. Sampling of Lake Ontario, conducted in 1972 at several near-shore and mid-lake sites, indicated the following:[14,15]

   PCB in fish (alewives, smelt, slimy sculpin) = $2.35 - 5.13 \times 10^6$ ppt.
   PCB in water (total concentration dissolved + particulate) = 55 ppt.
   Average PCB in sediments = 1.2×10^5 ppt.
   Average PCB in net plankton = 7.2×10^6 ppt.
   Average PCB in benthos = 4.71×10^5 ppt.

   It was assumed that these concentrations are the result of PCB accumulations at a constant rate for the past 40 years.

2. Determination of the rate of PCB deposition in the sediments:

   The average sedimentation rate of Lake Ontario is 1.2 mm/yr (as compared to a rate of 1.0 mm/yr for Lake Michigan.

   Therefore, the thickness of sediment today in Lake Ontario, after 40 years of deposition = 48 mm.

   At this constant rate of deposition, PCBs accumulate in the sediments at a rate = $\frac{1.2 \times 10^5 \text{ ppt PCB}/40 \text{ yrs}}{48 \text{ mm sediment}/40 \text{ yrs}} = 2.5 \times 10^3$ ppt PCB/mm of sediment

   $= 3 \times 10^3$ ppt PCB/yr.

3. Annual accumulation of PCBs in the biota =

$$= \frac{PCB_{fish} + PCB_{Plankton} + PCB_{benths}}{(3)(40 \text{ yrs})}$$

$$= \frac{(5.13 \times 10^6 \text{ ppt}) + (7.2 \times 10^6 \text{ ppt}) + (.471 \times 10^6 \text{ ppt})}{(3)(40 \text{ yrs})}$$

$= 0.11 \times 10^6$ ppt/yr.

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4. Annual accumulation of PCBs in the water = $\frac{55 \text{ ppt}}{40 \text{ yrs}}$ = 1.38 ppt/yr.

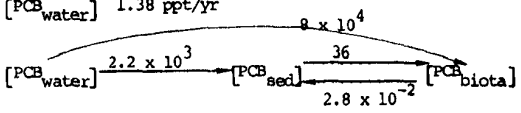
5. Concentration ratios of PCBs in the three phases are:

$$\frac{[PCB_{sed.}]}{[PCB_{water}]} = \frac{3 \times 10^3 \text{ ppt/yr}}{1.38 \text{ ppt/yr}} = 2.2 \times 10^3$$

$$\frac{[PCB_{biota}]}{[PCB_{sed.}]} = \frac{0.11 \times 10^6 \text{ ppt/yr}}{3.0 \times 10^3 \text{ ppt/yr}} = 36$$

$$\frac{[PCB_{biota}]}{[PCB_{water}]} = \frac{0.11 \times 10^6 \text{ ppt/yr}}{1.38 \text{ ppt/yr}} = 8 \times 10^4$$

Therefore,



6. Applying these ratios to Lake Michigan:

$$[PCB_{biota}] = [PCB_{water}](8 \times 10^4)$$
$$= (.078 \text{ ppb})(8 \times 10^4)$$
$$= 6.24 \text{ ppm}$$

$$[PCB_{sed.}] = [PCB_{water}](2.2 \times 10^3)$$
$$= (.078 \text{ ppb})(2.2 \times 10^3)$$
$$= 0.172 \text{ ppm}$$

C. Estimates of Plankton Biomass in Lake Michigan:

1. Assume a density of 300 kg. plankton/hectare of lake[16]
   Area of lake = 22,400 mi.^{2} = 5.8×10^6 hectare
   Therefore, plankton biomass = $(5.8 \times 10^6)(300 \text{ kg}) = 1.74 \times 10^{12}$g.
   $= 3.8 \times 10^9$ lb.

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D. Estimate of Flow of PCBs Through the Straits of Mackinac:

1. Water flows out of the lake via Straits at a rate = 67,000 cfs.
$= 1.3 \times 10^{14}$ lb of water/yr.

Using the concentration of PCB in the water as 0.013ppb,[17] the loss of PCBs through the Straits is: $= (1.3 \times 10^{14}$ lb/yr)(0.013 ppb)
$= 1.7 \times 10^{3}$ lb PCB/yr.

Assuming a constant loss over the past 40 years, 6.8×10^{4} lb of PCB would have been lost through the Straits.

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APPENDIX F

TOXICOLOGICAL ASPECTS

1.0 TOXICOLOGICAL ASPECTS OF POLYCHLORINATED BIPHENYLS (PCBs)

1.1 Introduction

A critical biological effect of polychlorinated biphenyls (PCBs) is the induction of tumors in mice and rats, which implies potential human activity. Cancer is typically progressive and irreversible, in the absence of medical intervention. Virtually all chemicals known to cause cancer in man have been shown to cause tumors in animals, including mice and rats. The use of experimental animals to test chemicals is generally accepted as a reliable basis for estimating potential carcinogencity to humans. Pathological development of chemically induced tumors in experimental animals and in humans is very similar, and most of the major types of human cancer can be reproduced in animals by chemical induction. Mice and rats are generally the preferred experimental animals because their relatively short lifespan permits lifetime testing within two to three years, whereas chemical carcinogenesis in humans is usually manifested by a latent period of 30 to 40 years between exposure and the appearance of symptoms. This long latency period coupled with the lack of adequate human data, and the lack of identifiable control groups for widespread agents such as PCBs, make it difficult to identify PCBs as a "human" carcinogen by conventional epidemiological studies. However, most experts in chemical carcinogenesis, including researchers at the National Cancer Institute of NIH and the World Health Organization, accept animal data as predictive of potential human activity.

To date, no minimum effective dose or maximum safe dose has been established for carcinogenic chemicals in man or animals; therefore in approaching the problem of formulating regulatory action all mammalian systems are considered sensitive and man must be considered the target system.

Although in at least one positive study on PCBs the dosage level used would be considered low, high levels are generally used in animal tests because the limited number of animals may render the tests relatively inconclusive. In addition, the strain or species used may also render the tests comparatively insensitive. Failure to demonstrate response at low doses of an oncogen is not an adequate basis to establish a "no-effect" level.

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Virtually no chemical that has been adequately studied is known to cause only benign tumors. Furthermore, oncogens may cause tumors at different sites in different animals species or strains depending upon factors such as routes of metabolism and excretion.

In considering the current status of medical knowledge, a lack of understanding of the carcinogenic mechanism within cellular biochemistry is evident. One issue that must be resolved in order to establish effective control legislation is whether or not there is a level of carcinogenic exposure below which there are no effects.

The two points of view are known as the "threshold" and the "no-threshold" concepts. The threshold concept is based on the theory that there is a dose level below which no effect will occur regardless of the number of test animals exposed; since this no-effect dose level would be higher than any resultant legally-established exposure limit, humans would not be harmed by doses at or below the limit. The assumption is made that the number of animals affected will decrease at a greater rate than the rate of decrease in the dose until a zero-point is reached. This assumption is unverified. Proponents of the threshold concept believe that for every toxic chemical there is an exposure level below which no effect can occur in a given organism, and that no effect, or possibly even beneficial effects at subthreshold doses, gives way to undesirable effects as the dose is raised. No valid data have been developed to support the concept of safe levels of exposure to carcinogens since the extremely large numbers of animals needed for such experiments preclude such testing, and extrapolation of animal data to man is tenuous.

The no-threshold proponents insist that any substance which is carcinogenic at any level must be regarded as such at all levels. They further insist that it is not possible to predict safe levels of carcinogens based on an arbitrary fraction of the lowest effective animal dose, regardless of how many test animals are used. For those chemicals which have been shown to be carcinogens in experimental animals, no thresholds have been demonstrated. Thus neither the no-threshold theory (or zero-dose concept) nor the threshold concept can be demonstrated or disproved at the present time.

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In the development of a standard for a carcinogen, the following recommendations, taken from the April 22, 1970 report to the Surgeon General by the Ad Hoc Committee on the Evaluation of Low Levels of Environmental Chemical Carcinogens, National Institutes of Health, should be considered:

1. No level of exposure to a chemical carcinogen should be considered toxicologically insignificant for man. For carcinogenic agents, a 'safe level for man' cannot be established by application of our present knowledge. The concept of 'socially acceptable risk' represents a more realistic notion.

2. The principle of a zero tolerance for carcinogenic exposures should be retained in all areas of legislation presently covered by it and should be extended to cover other exposures as well. Only in the cases where contamination of an environmental source by a carcinogen has been proven to be unavoidable should exception be made to the principle of zero tolerance. Exceptions should be made only after the most extraordinary justification, including extensive documentation of chemical and biological analyses and a specific statement of the estimated risk for man, are presented. All efforts should be made to reduce the level of contamination to the minimum. Periodic review of the degree of contamination and the estimated risk should be made mandatory.

3. A basic distinction should be made between intentional and unintentional exposures.

   (a) No substance developed primarily for uses involving exposure to man should be allowed for wide-spread human intake without having been properly tested for carcinogenicity and found negative.

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(b) Any substance developed for use not primarily involving exposure in man but nevertheless resulting in such exposure, if found to be carcinogenic, should be either prevented from entering the environment or, if it already exists in the environment, progressively eliminated.

The same report states:

> The production of specific carcinogenic chemicals for uses that do not primarily involve an intentional exposure of man, but which result in such environmental contamination that extensive human exposure becomes inevitable, must also be controlled. The most effective prevention of exposure in man is the elimination of carcinogen production, or control of entry into the environment.

More recently, the Subcommittee on Estimation of Risks of Irreversible, Delayed Toxicity to the Department of Health, Education and Welfare Committee to Coordinate Toxicology and Related Programs published their report (Hoel et al, J. Toxicol. Environ. Health 1, 133, 1975).

> The Subcommittee suggests (on an interim basis only) a computational procedure to assist in setting levels of qualitatively unavoidable chemicals (both natural and manmade) in the environment compatible with a socially acceptable level of risk. It includes a simple arithmetic procedure to compute an exposure dose of a chemical for humans so that there will be a high probability that this dose will give a risk equal to or below the specified level.
>
> Data from experiments designed to detect irreversible self-replicating changes (carcinogenesis) in experimental animals will be used. Through this arithmetic, the results will be translated to appropriately low levels for humans. In

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addition, human exposure data need to be considered. All the knowledge necessary to evaluate these factors does not yet exist. We suggest here an interim procedure to be used until research points to better procedures such as methods for obtaining direct or best estimates of risk at a given dose with their corresponding confidence limits. Some of this research is now under way. These suggestions must be reviewed as new research is available, but not longer than within two years.

Specifically, the so-called linear straight-line arithmetic method combined with a 99% confidence level for extrapolation to very low levels works this way:*

1. Say an experiment at a dose, d, using 100 animals has shown no induced tumors, for example, in the animals, that is, 0/100≈0%.

2. The upper 99% confidence limit on this result (which can be found in standard statistical tables) is 0.045, that is, 4.5%.

3. For a dose, d_s, that will produce, as an upper limit, fewer than 1 in 1,000,000 tumors, divide 1/1,000,000 by .045. This gives (in standard notation) $2.22 \times 10^{-5} d$ as the appropriate dose. If one were to aim for fewer

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* For certain compounds, some knowledge of the carcinogenicity process may be available, such as with renal concretions resulting in bladder tumors. In these instances, models other than the linear model may be more appropriate.

For illustration we consider only the case of one experimental dose. In practice, however, it is expected that several dose levels will be available and their treatment can be found in the literature (Gross et al., 1970; Mantel and Bryan, 1961; Mantel et al., 1975).

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than 1 in 100,000,000, (i.e., 1×10^{-8}), the appropriate dose would be $2.22 \times 10^{-7}d$; for fewer than 1 in a hundred thousand (1×10^{-5}), the appropriate dose is $2.22 \times 10^{-4}d$, etc. If 10 of the 100 animals showed a response (i.e., 10/100 = 10%), then the 99% confidence limit is 0.19, that is, 19%. The appropriate dose for 1 in a million is then $5.3 \times 10^{-6}d$ and for 1 in 100,000,000, the dose would be $5.3 \times 10^{-8}d$.

For corrections to a 'natural' incidence, the normal distribution is used to approximate a 99% confidence interval on the difference between the response at dose d and the background. Suppose at dose d 60 of 200 (30%) animals were affected while the natural incidence gave 20 of 200 animals (10%). The upper 99% confidence limit is then approximately

$$.3 - .1 + 2.327[.3(.7)/200 + .1(.9)/200]^{1/2} = 0.29$$

where 2.327 is the 99% point of the standard normal distribution. For a dose, d_g, that will produce as an upper limit of fewer than 1 in a million changes in excess of the natural incidence, 1/1,000,000 is divided by 0.29. This gives $3.4 \times 10^{-6}d$ as the dose, and for 1 in 100,000,000 excess changes the dose is $3.4 \times 10^{-8}d$.

Two questions need to be answered in converting results in animals to man:

1. In what units should the dose conversion be made (i.e., weight basis, surface basis, etc.)? At present it appears that the appropriate dose unit is the 'surface' unit, that is, use the 2/3 power of the weight of the two species (test animal-man) as the surface area conversion factor. For example, if a 25-g mouse receives a dose stated on a milligram basis, then the corres-

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ponding dose (mg) for a 70-kg man would be (70 kg/25g)$^{2/3}$ = 200 times the mouse dose. Thus, on a mg/kg basis, the use of surface units would require that the corresponding relative dose become (70 kg/25 g)$^{1/3}$ = 14 times the mouse dose. Dose expressed in concentration (ppm) should lead to approximately the same levels as dose expressed in surface area units.

2. Should any additional safety factor be added in going from animals to man? Yes, but not the same factor for all substances. This species conversion factor should be determined substance-by-substance using appropriate biological considerations (and allowing for any safety factors implicit in other parts of the calculation).

A statutory provision exists, however, which provides some sanction to the no-threshold concept. This is, of course, the "Delaney clause", Section 409(c) (3) (A) of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 321 et seq.), which became law in 1958. This clause provides "... that no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaulation of the safety of food and additives, to induce cancer in man or animal..."

In spite of all of the furor concerning this clause, it is interesting to note that since its introduction in 1958, it has been invoked only twice to ban food additives and both of these were trivial components of food packaging.

The Food and Drug Administration, in addition to its responsibility for regulating food additives, is also supposed to protect the public from carcinogens which appear naturally or incidentally in our food. These substances are not covered by the Delaney clause. Aflatoxins, DDT, aldrin, nitrosamines, and vinyl chloride are examples. Presently, these problems are handled on the basis of practicality and not on any assessment of risk. That PCBs presently exist in our diet has been amply demonstrated. But the pressure to eliminate such carcinogens from entering our food must fall upon other regulator agencies such as EPA.

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In summary, there is no generally accepted toxicological basis upon which to establish a no-effect level for any carcinogenic material. Methods which arrive at estimates of acceptable exposure levels for carcinogens in man are, therefore, based on the concept of a "socially acceptable level of risk." In general, the methods employ statistical extrapolation of laboratory animal test data to man, whereupon a political decision as to the socially acceptable incidence of tumors is made. Such estimates of socially acceptable level of risk to determine human exposure tolerances to ionizing radiation have been employed by the Atomic Energy Commission and adopted by the Environmental Protection Agency. Estimates based on acceptable level of risk are only conceptual and must not be taken as calculated no-effect levels.

1.2 Mammalian Toxicity

The current knowledge of the interaction of PCBs with life forms will not be reviewed in detail in this report; an exhaustive review will be submitted in the final report on Task I. This report will highlight only those data relating tumor induction. This review, however, is complete in the sense that major adverse effects are mentioned including those within the major target organs.

PCBs have low acute toxicity. But because of their near complete absorption, high lipid (fat) solubility, low water solubility, and relative chemical inertness, PCBs tend to concentrate in the food chain, accumulate in body fat, persist in biological tissue, and show persistent toxicity. Consequently, short-term studies are not adequate indicators of the long-term effects of PCB exposure. Latent effects, those effects that occur some time after exposure has ceased, and cumulative effects, those effects that occur only after a threshold level of PCB or tissue damage has been reached, may be easily missed over the short term. Since most toxicity studies with PCBs have been short-term, there is limited scientific evidence establishing or predicting the chronic effects.

1.2.1 Subacute and Chronic Toxicity

"No-effect" levels of PCBs in rats and dogs fed three Aroclors for two years were reported by Monsanto in 1971. A summary of their results is presented here.

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Rats - Method

A two-year chronic toxicity study was conducted using rats fed diets containing Aroclors 1242, 1254 and 1260. The animals employed in the test were Charles River strain albino rats. Four hundred rats (200 male and 200 female) were selected for each of the experiments.

Outline of Each Experiment

Group	Number of Animals		Dietary Level (ppm)
	Male	Female	
Control	50	50	None Administered
T-I	50	50	1
T-II	50	50	10
T-III	50	50	100

Rat Results - Aroclor 1242

At sacrifice after 3, 6 or 12 months on test, organ weights, organ to body weight and organ to brain weight ratios disclosed several randomly occurring intergroup differences. The lack of any consistent dose-related response and the absence of any deleterious tissue changes confirm that these differences were not related to the ingestion of Aroclor 1242.

At the final sacrifice after 24 months on test, the liver weights and liver to body weight or brain weight ratios were significantly elevated in females from the T-III group. Histologic examination of the livers from the T-III group revealed several animals with vacuolar changes indicative of fatty degeneration. Specific fat stains confirmed the presence of fat in these vacuoles. Focal hypertrophy and focal hyperplasia were also found in the livers from animals fed Aroclor 1242.

Hyperplasia of the urinary bladder was found in animals from the control group and from each of the test groups. This hyperplasia was usually associated with cystitis.

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The incidences and types of all tumors were about the same in all groups, including the control group, and are considered normal for rats of this age.

Rat Results - Aroclor 1254

At sacrifice after 3, 6, or 12 months on test, organ weights, organ to body weight and organ to brain weight ratios disclosed several randomly occurring intergroup differences. The lack of any consistent dose related response and the absence of any deleterious tissue changes confirm that these differences were not related to the ingestion of Aroclor 1254.

At the final sacrifice after 24 months on test, the absolute liver weight and liver to body weight or brain weight ratios were significantly elevated in both T-III males and females. Histologic examinations of the livers from the T-III group revealed several animals with vacuolar changes indicative of fatty degeneration. Specific fat stains confirmed the presence of fat in these vacuoles. Focal hypertrophy and focal hyperplasia were also found in the livers from animals fed Aroclor 1254.

Hyperplasia of the urinary bladder was found in animals from the control group and from each of the test groups. This hyperplasia was usually associated with cystitis.

None of the tumors found could be related to the ingestion of Aroclor 1254 and are considered normal for a random population of rats this age.

Rat Results - Aroclor 1260

At sacrifice after 3, 6, or 12 months on test organ weights, organ to body weight and organ to brain weight ratios disclosed several randomly occurring intergroup differences. The lack of any consistent dose related response and the absence of any deleterious tissue change confirm that these differences were not related to the ingestion of Aroclor 1260.

At the final sacrifice after 24 months on test, the liver weights and liver to body weight or brain weight ratios were significantly elevated in the rats from the T-III group. Histologic examination of the livers from the T-III

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group revealed several animals also with vacuolar changes indicative of fatty degeneration. Specific fat stains confirmed the presence of fat in these vacuoles. Focal hypertrophy and focal hyperplasia were also found in the livers from animals fed Aroclor 1260.

Hyperplasia of the urinary bladder was found in an animal from the control group but not in any of the test animals.

The incidences and types of all tumors were about the same in all groups, including the control group, and are considered normal for rats of this age.

Dogs - Method

The two-year toxicity study utilized an untreated control group and three test groups, each consisting of eight purebred beagle dogs (four males and four females). The beagles were all eligible for A.K.C. registration and had been previously immunized.

The material to be tested, Aroclors 1242, 1254,aand 1260 were incorporated into a stock diet and fed to the dogs seven days a week in three graded dietary levels. The levels were 1, 10 and 100 ppm.

An outline of the test organization is presented here:

Outline of Each Experiment

Group	Number of Animals		Dietary Level (ppm)
	Males	Females	
UC	4	4	None
I	4	4	1
II	4	4	10
III	4	4	100

Dog Results - Aroclor 1242, 1254 and 1260

No significant abnormalities were observed in the following parameters:

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Body Weight
Food Consumption
Behavioral Reactions
Hematology
Urine

Animals receiving 100 ppm of Aroclor 1260 exhibited increases in serum alkaline phosphatase activity at the conclusion of the investigation.

A female receiving 100 ppm of Aroclor 1242 was sacrificed *in extremis* after 60 weeks of testing; gross and histologic examinations revealed severe chronic peritonitis. A male receiving 10 ppm died after 32 weeks of testing; death was attributed to chronic pneumonia. Histologic examination revealed no abnormalities related to the test material ingestion.

Two fatalities occurred during the Aroclor 1254 study: a 100 ppm female after 33 weeks of testing and a 10 ppm female after 37 weeks. The female receiving 100 ppm died from injuries received in a fight. Gross and histologic examinations of the 10 ppm female revealed chronic peritonitis.

Two fatalities occurred during the Aroclor 1260 study: a 100 ppm female after 29 weeks and a 100 ppm male after 33 weeks. Gross and histologic examinations revealed severe chronic peritonitis in the female and acute pneumonia in the male.

All animals receiving 100 ppm of Aroclor 1260 exhibited elevations in liver to body weight ratios.

Gross and histologic examination of all remaining animals revealed no significant abnormalities.

Work by Dr. James Allen (U. of Wisconsin) on simians is discussed in the following paragraphs.

Simians - Method

The hazards to simians of low level PCB exposure have been demonstrated only very recently. Allen in 1974 reported the results of feeding

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six adult female rhesus monkeys a diet containing 25 ppm of Aroclor 1248 for two months. The average total intake of PCBs for five animals fed for two months was approximately 250 mg, or 0.78 mg/kg body weight per day. The sixth monkey consumed a total of 450 mg at 1.34 mg/kg/day; this animal died 68 days after feeding was stopped.

The effects in all six animals included facial swelling, severe hyperplastic gastritis and liver necrosis. All but one of the surviving were unable to conceive. The one live birth was a smaller than average infant.

The surviving monkeys continued to have high adipose tissue levels, acne, tissue swelling and hair loss two years after this short term, low level exposure. As will be seen, these signs were similar to those encountered in humans during the "Yusho" intoxication in Japan (described later in this report).

1.2.2 Reproduction

PCBs have been shown to affect reproduction in several different species. Egg production, egg hatchability, and shell thickness were decreased by feeding low levels of various PCB formulations to chickens. Female rats fed 20 ppm of Aroclor 1254 (1.5 mg/kg/day) had a decrease in the number of litters and in litter size. In a two-generation study, 5 ppm was the no effect level for rat reproduction. Higher dietary levels caused decreased rat offspring survival and decreased mating performance. Even at 1 ppm, male rats were born with enlarged livers. In a more recent study, Allen has reported that levels in the diet as low as 2.5 ppm resulted in a marked decrease in the ability of monkeys to conceive.

1.2.3 Pathology

One of the most studied toxic effects of PCBs has been in liver pathology in rats and rabbits. PCBs cause similar damage when administered by injection, inhalation, or by mouth. In cases of PCB poisoning, early liver damage has been noted. Many researchers have described the now classical pathological changes in the liver of animals exposed to PCBs. These include infiltration by fat, increased cell and liver size, degeneration of cellular contents, and ultimately cell death. The latent nature of these effects is demonstrated by the fact the most severe histopathology known occurred 5 to 13 weeks after PCB ingestion had ceased.

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Additional pathological changes have recently been noted. These were classified as adenofibrosis and are often seen in association with liver carcinoma. Abnormal growth and development of the gastric mucosa has also been reported and is further evidence of the carcinogenic potential of PCBs.

For reasons completely independent of any possible association with cancer, the significance of fibrosis, adenofibrosis, and liver necrosis are very grave. These lesions may be associated with carcinomas in rodent liver.

1.2.4 Carcinogenicity

Unfortunately, statistically sound dose-carcinogenic response studies necessary to treat many environmental problems, including PCBs, are currently not available. A review of the world scientific literature reveal only six studies pertinent to carcinogenesis. These are listed and discussed below.

1. Kimbrough, R.D., Linder, R.E., and Gaines, T.B., "Morphological Changes in Livers of Rats Fed Polychlorinated Biphenyls", Arch. Envon. Health 25, 354 (1972).

   An extensive chronic study of Sherman rats, using Aroclors 1260 and 1254, with dietary levels of 0, 20, 100, 500 and 1000 ppm, documented a variety of histopathological effects after 8 months of exposure. Degenerative liver changes observed in both male and female test animals at all dosages of both PCBs included hypertrophy of individual liver cells, hyperchromatic pleomorphic nuclei, cytoplasmic lipid vacuoles, and porphyria, all characteristics of chlorinated hydrocarbon (DDT, dieldrin) intoxication. In some cases, adenofibrosis (uncertain significance) was observed. All of the mortalities that occurred during exposure to the Aroclor 1260 were female. In nearly all gross

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pathological examinations, males demonstrated enlarged livers, while females did not; liver effects of Aroclor 1254 were adjudged more pronounced than those of Aroclor 1260.

The short duration of this study is a drawback for its inclusion in evaluation of carcinogenic effects.

2. Kimura, N.T. and Baba, T., "Neoplastic Changes in the Rat Liver Induced by Polychlorinated Biphenyl", Gann 64, 105 (1973).

Following the observation, by electron microscopy, of specific morphological alterations (previously observed with other carcinogens) in liver cell nucleoli of animals ingesting PCBs, a preliminary study on PCB carcinogenic activity was instituted. Using rats of the Donry strain, Kanechlor 400 mixed in oil was fed at dietary levels ranging upwards from 38.5 ppm. Ten male and ten female rats were in the experimental group with five of each sex in the control group. Using body weight gains (compared to controls) the concentration of the Kanechlor was increased or decreased according to the following schedule.

Period of Feeding (days)	Concentration of Kanechlor-400 (ppm)
26	38.5
57	77
21	154
21	308
56	616
39	462
29	0
98	462
28	0
82	462
Total 400	

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Multiple adenomatous nodules were observed in all livers of the female experimental group ingesting more than 1200 mgs of Kanechlor 400. In sharp contrast, however, the liver specimens of the male experimental rats revealed no such changes even in animals receiving comparable or higher amounts of Kanechlor 400 than females. Although these authors refer to this lesion as benign in nature, further discussion of this lesion is presented later in this report.

The variable dosage schedule and the small numbers of animals used present drawbacks for its inclusion in evaluation of carcinogenic effects.

3. Ito, N., et al. "Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and its Promoting Effect on Liver Tumors Induced by Benzene Hexachloride", J. Natl. Cancer Inst., 51, 1637 (1973).

   This paper reports the histopathologic and ultrastructural observations of livers of dd mice fed PCBs in their diet for a period of 32 weeks. Twelve male mice were used at each of three dosage levels. Three PCBs were investigated, Kanechlor 500, 400, and 300. The results indicate hepatocellular carcinomas and nodular hyperplasia were induced by Kanechlor 500 but not by the two other PCBs, as seen below:

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PCBs Diet (ppm)	Cellular Hypetrophy	Nodular Hyperplasia	Hepatocellular Carcinoma
Kanechlor 500 (500)	++	7/12	5/12
Kanechlor 500 (250)	+	0/12	0/12
Kanechlor 500 (100)	±	0/12	0/12
Kanechlor 400 (500)	++	0/12	0/12
Kanechlor 400 (250)	+	0/12	0/12
Kanechlor 400 (100)	±	0/12	0/12
Kanechlor 300 (500)	±	0/12	0/12
Kanechlor 300 (250)	±	0/12	0/12
Kanechlor 300 (100)	-	1/12	0/12
Control	-	0/6	0/6

The effect of PCBs on neoplastic changes induced by isomers of benzene hexachloride (α, β and γ) in the livers of mice fed a diet containing BHC with and without PCBs for 24 weeks was also studied. The authors concluded that in addition to the carcinogenic activity of PCBs, these materials, also promote tumors induced by α BHC and β BHC.

4. Kimbrough, R.D., and Linder, R.E., "Induction of Adenofibrosis and Hepatomas of the Liver in BALB/cj Mice by Polychlorinated Biphenyls (Aroclor 1254)", J. Natl. Cancer Inst., 53, 547 (1974).

Two groups of 50 BALB/cj inbred male mice were fed 300 ppm of Aroclor 1254 in the diet for 11 and 6 months. The six-months group was given a recovery period of 5 months. The results are presented below:

Dietary Level (ppm)	Exposure Time (Mo.)	Total Survivors	Hepatoma
0	0	34	0
0	0	24	0
300	11	22	9
300	6	24	1

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In addition, all 22 mice in the group receiving Aroclor 1254 demonstrated adenofibrosis which was not observed in any other group.

5. Makiura, S., et al, "Inhibitory Effect of Polychlorinated Biphenyls on Liver Tumorigenesis in Rats Treated with 3'-Methyl-4-Dimethylaminoazobenzene, N-2-Fluorenylacetamide, and Diethylnitrosamine", J. Natl. Cancer Inst., 53, 1253 (1974).

   The effect of PCBs (Kanechlor 500) on liver carcinogenesis induced by 3-methyl-4 dimethylaminoazobenzene (3' Me-DAB), N-2-fluorenylacetamide (2-FAA) and/or diethylnitrosamine (DEN) was studied in male Sprague-Dawley rats. Duration of exposures were 20 weeks. Liver tumors developed with the three known liver carcinogens, i.e., 3' Me-DAB, 2 FAA, and DEN. No tumors developed in the animals fed PCBs alone and when fed with the above mentioned carcinogens a marked reduction in tumor incidence was observed. The lack of tumors in the PCBs fed rats may have been the result of low dose (500 ppm) and/or the short period of administration since these same authors had induced tumors in rats treated with Kanechlor 500 at 1000 ppm for 72 weeks. Histopathology findings of the livers were similar as previously reported; i.e., fatty changes and cell hypertrophy.

6. Kimbrough, R.D.; Squire, R.A.; Linder, R.E.; Strandberg, J.D.; Montali, R.J. and Burse, V.W., "Induction of Liver Tumors in Rats by Polychlorinated Biphenyl Aroclor(R) 1260", J. Natl. Cancer Inst. (in press, 1975).

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Two hundred Sherman Strain female rats were fed 100 ppm of polychlorinated biphenyl (Aroclor 1260) for approximately 21 months, and 200 female rats were kept as controls. The rats were sacrificed when 23 months old. Twenty-six of 184 surviving experimental rats and 1 of 173 surviving control rats examined had hepatocellular carcinomas. None of the controls, but 146 of the 184 experimental rats, had neoplastic nodules in their liver. Areas of hepatocellular alteration were noted in 28 of the 173 controls and 182 of the 184 experimental rats. It was concluded that Aroclor 1260 had a hepatocarcinogenic effect in female Sherman Strain rats. The incidence of tumors in other organs did not differ appreciably between the experimental and control groups.

1.2.5 Bryan-Mantel and One Hit Model Calculations of Animal Data for Extrapolation to Humans

As indicated previously, statistical handling of experimental data helps resolve questions of experimental design and the problems of threshold in setting safe doses. We have applied the Bryan-Mantel and One Hit Model calculati to two studies. The results of these analyses are presented in Tables I and II.

Therefore, using the recommendations set forth previously, we conclude that the use of the Bryan-Mantel Probit Model should be used to calculate the "safe" level of PCBs using a theoretical maximum acceptable lifetime risk of $1/10^6$ of development of hepatomas (neoplastic nodules). This dose is 167 ppt at the 99-percent confidence limits if the latest data in rats (Kimbrough 1975) is used. In the case of development of hepatocarcinomas, the level would be 11,887 ppt.

The rather low "safe" dose relative to the hepatomas reflects that the dosage level used in the experiment (i.e., 100 ppm) was too high for that response (146 hepatomas in 184 rats). These neoplasms are mostly benign tumors

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Table I

Analysis of Carcinogenic Risk to Humans from Ingested PCBs Based on Kimbrough 1975 Study (Rats)

Analytical Method	Confidence Limits (%)	Intake Level in ppt for Specified Levels of Risk for Hepatocarcinomas $1/10^{8}$*	$1/10^{7}$*	$1/10^{6}$*	$1/10^{5}$*
Bryan-Mantel	95	1963	5080	14,187	43,640
Bryan-Mantel	99	1645	4257	11,887	36,566
One Hit	95	4	45	447	4,472
One Hit	99	4	39	391	3,906

Analytical Method	Confidence Limits (%)	Intake Level for ppt for Specified Levels of Risk for Neoplastic Nodules $1/10^{8}$	$1/10^{7}$	$1/10^{6}$	$1/10^{5}$
Bryan-Mantel	95	27	70	197	605
Bryan-Mantel	99	23	60	167	512
One Hit	95	0	2	21	205
One Hit	99	0	2	18	180

Analytical Method	Confidence Limits (%)	Intake Level for ppt for Specified Levels of Risk for Foci $1/10^{8}$	$1/10^{7}$	$1/10^{6}$	$1/10^{5}$
Bryan-Mantel	95	0	1	3	10
Bryan-Mantel	99	0	1	2	6
One Hit	95	0	0	0	3
One Hit	99	0	0	0	1

*Risk level of one tumor per 10^{8}, 10^{7}, 10^{6}, or 10^{5} population

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Table II

Analysis of Carcinogenic Risk to Humans from Ingested PCBs based on Kimbrough-1974 Study (Mice)

Analytical Method	Confidence Limits (%)	Intake Level in ppt for Specified Level of Risk for Hepatoma (Neoplastic Nodules) $1/10^{8*}$	$1/10^{7*}$	$1/10^{6*}$	$1/10^{5*}$
Bryan-Mantel	95	451	1167	3258	10022
	99	297	768	2145	6597
One Hit	95	2	21	214	2140
	99	2	16	160	1596

*Risk level of one tumor per 10^8, 10^7, 10^6, or 10^5 population.

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occurring late in life. There is little time left for them to become malignant in the remaining life-time of the rat. Until further data become available or other means are used to handle existing data, one should assume the "safe" dose in lifetime human diet to be between 0.2 ppb and 12 ppb.

It is interesting to note that if the simian reproduction data is used and the classical 1/100 safety factor is applied to the lowest dose studied (2.5 ppm), a "safe" dose of 25 ppb is obtained. This dose (2.5 ppm), however, appears to be a minimal effective dose, whereas normally the highest no-effect level is used. Use of minimum effect levels and even other safety factors have been used; e.g., 1/10 to 1/5000. These would result in dosage levels ranging from 250 ppb to as low as 0.5 ppb.

These calculations must be considered preliminary since time has not permitted consideration of other factors, such as:

1) Body surface area instead of body weight in determining daily intake
2) Comparison with most likely human daily intake
3) Further calculations of existing data
4) Combination of all existing animal data
5) Consideration of metabolism, storage and excretion data among animals species as compared to man

1.3 Observations in Humans

In addition to data provided by continuing studies of the various effects of PCBs on laboratory animals, some information is available on the subacute or chronic effects of PCBs on humans.

Human intoxication with Kanechlor 400, a PCB manufactured in Japan (48-percent chlorine) was observed after a heat exchanger leaked fluid into rice oil which was then consumed by Japanese families in 1968. Approximately 1,000 persons were affected, and typical clinical findings included:

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1. Increased eye discharge
2. Acne-like eruptions
3. Dark brown pigmentation of nails
4. Pigmentation of skin
5. Transient visual disturbance
6. Feeling of weakness
7. Numbness in limbs
8. Headache
9. Weight loss
10. Vomiting
11. Diarrhea
12. Fetal toxicity

Items 5 through 8 represent symptoms of damage to the nervous system seen in "Yusho" patients. PCBs are known to enter the brain, but they do not have a predominant central neurotoxic effect like the related hexachlorophene.

Laboratory findings in the severe cases included:

1. Red blood cells and hemoglobin decreased; leukocytes increased
2. Total serum lipids, triglycerides, alpha 2-globulins increased
3. Slight increase in alkaline phosphatase
4. Liver biopsy-reduction of rough endoplasmic reticulum; hypertrophy of smooth endoplasmic reticulum; giant mitochondria were frequently encountered

When 159 "Yusho" patients were examined in 1969 and 1970, it was found that 50 percent showed no clinical improvement and 10 percent were worse, another indication of the persistence of PCBs in the human body. The chemical was found to be stored primarily in the adipose tissue but also passed into the placenta and fetus.

A very early and common symptom in these patients was chloracne. Chloracne is an occupational skin disease caused by many chemicals. Chloracne resembles adolescent acne in some ways, but is generally more severe. Its symptoms consist of comedones with or without cysts and pustules. The openings of the hair

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follicles are filled with oil and protein material. Darkening of the skin and secondary inflammation may also occur. During the 1930s and 1940s several large outbreaks occurred in workers engaged in the manufacture of PCBs and closely related chemicals.

The disease can be produced by both direct skin exposure and by oral intake of PCBs. The ability of oral consumption of PCBs to cause persistent chloracne was convincingly demonstrated in the "Yusho" incident, where chloracne was still present in several people three years after oral consumption of PCBs had ceased.

The same study showed no significant difference among sexes, but a significant difference in clinical severity by age was observed, with the 13- to 29-year-old group being the most sensitive. Of the 11 babies born to affected mothers, 2 were stillborn, 9 had dark-brown stained skin, and increased eye discharge was noticeable in most. Growth rates of affected children, as measured by both height and weight gains, were monitored and compared with unaffected classmates; a significant decrease in growth rate was detected in the males who were poisoned, but no definitive change was observed in the females.

Rice oil exposure levels were calculated at approximately 15,000 mg/day (average); the oil itself was reported to be contaminated at about 2,000 ppm Kanechlor 400 (derived from the known organic chlorine content of rice oil in relation to the known organic chlorine content of the PCB). The average total dose of PCBs causing an effect in these victims was reported as 2,000 mg. The lowest PCB level that produced human effects (50 kg man) was 500 mg consumed over a period of 50 days at a rate of approximately 200 ug/kg/day. The effect level was based, however, on overt symptoms, rather than on sensitive biochemical indicators that might have demonstrated effects at even lower levels. Since PCBs probably have a long biological half-life in humans, a toxicological analysis of the human data must be based on the assumption that ingested PCBs would continue to accumulate in tissues for a long period of time.

The apparent human health threat from chronic ingestion of PCBs prompted the U.S. Food and Drug Administration to issue proposed limitations on the levels

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of PCBs in foods, animal feeds, and food packaging materials. On July 6, 1973, final regulations were promulgated that established temporary tolerances for PCB residues arising from unavoidable contamination. These tolerances are:

1. 2.5 ppm in milk (fat basis)
2. 2.5 ppm in manufactured dairy products (fat basis)
3. 5 ppm in poultry (fat basis)
4. 0.5 ppm in eggs
5. 0.2 ppm in finished animal feed for food-producing animals (except the following finished animal feeds: feed concentrates, feed supplements, and feed premixes)
6. 2 ppm in animal feed components of animal origin, including fishmeal and other by-products of marine origin and in fish animal feed concentrates, supplements, and premixes intended for food-producing animals
7. 5 ppm in edible portions of fish and shellfish (the edible portion of fish excludes head, scales, viscera, and inedible bones)
8. 0.2 ppm in infant and junior foods
9. 10 ppm in paper food-packaging material intended for or used with human food, finished animal feed and any components intended for animal feeds (the tolerance does not apply to paper food-packaging material separated from the food by a barrier impermeable to migration of PCBs)

1.4 Conclusions

PCBs localize in certain tissues and do not break down easily in the body. This persistence leads to cumulative toxicity. Early toxicological evidence concerning the chronic adverse health effects of PCBs from experimental animals such as mice and rats and from observational data in humans has been more recently

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supplemented by additional experimental findings in monkeys. A close correlation exists between the symptoms noted in humans and those noted in the monkeys, suggesting that the dose response relationships and metabolic and excretion phenomena of PCBs are similar in both humans and monkeys. According to some pathologists, PCB exposure can cause cancerous liver lesions.

Evidence from relatively short-term exposure (several months) and chronic exposure in animals or humans demonstrates that PCBs are a significant health hazard.

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2.0 INTRODUCTION

Although unattainable, absolute safety (i.e., absolute control) is the goal society would like to achieve with regard to all chemicals introduced by industry. Safety as practiced, however, always entails some degree of risk. But experience has shown that maximization of chemical, physical, and toxicological information will minimize risk. For example, if a given compound is known to end up in man's food supply, information on its chemistry and potential chronic toxicity would be essential to minimizing the public health hazard.

The experience with PCBs illustrates the enormous range of complexity of risk evaluation that many new compounds may require for maximum public safety. We believe no one could have foreseen the present situation with PCBs. Thus we strongly feel all substances should not be subjected to a single rigid routine of study, as such action would be self defeating.

Instead, we propose that an orderly step-wise approach be made. Information gathered on specific chemicals should show the direction for the acquisition of additional information. The continuous use and especially the increasing use of new chemicals should be paralleled by additional testing of the chemicals. Such a hierarchy or sequential testing will: (1) result in avoidance of unnecessary test procedures and (2) answer those questions which will in the long run reveal the most productive information.

2.1 Estimation of Dose to the Target System

Mass production of chemicals invariably results in some degree of environmental contamination, but the route by which a given contaminant affects humans varies according to the type of compound. Vinyl chloride, for instance, presents a hazard almost entirely on the occupational level - that is, among workers dealing with vinyl chloride. For PCBs, on the other hand, exposure through direct contact is not the issue; bioaccumulation through the food chain is the exposure route of interest.

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The pattern of use is one of the most significant factors in determining the exposure of the target system. The use of PCBs in carbonless paper prior to the voluntary ban on this use in 1971 has proven to be an excellent example of the devious routes by which pollutants find their way into our food — carbonless paper is recycled to paperboard for food packaging, and, in addition to PCB release to the waterways during the recycling process, the paperboard itself leaches PCBs to food it contains.

The method of disposal of waste also presents problems, especially with such highly stable compounds as PCBs. Ease of disposability and rapid decomposition to inert compounds after disposal are characteristics which are highly desirable in substitutes for PCBs.

For some PCB substitutes an elaborate examination of their movement through the environment, their transformation by chemical, physical or biological interactions and the dissemination and transport of the resultant compounds may be essential.

The nature of injury must be considered. A reversible functional effect, though undesirable, would be of vastly less consequence than irreversible and fatal effects. Mutagenesis and teratogenesis are more subtle forms of injury, but the testing methods for these grave threats generally are elaborate and involved. This field, however, is advancing rapidly.

With respect to wildlife, considerations are substantially different than with man. Because of the impossibility of pretesting all species with all new chemicals, concern must of necessity be on the endangerment of a species or of a local animal population. This type of information frequently can only be obtained by constant surveillance of the environment within which a compound is released.

2.2 Nature of Tests Needed to Evaluate Human Health Effects

The major determinants of the effects of chemicals upon the health and well-being of the individual and society are:

1. The nature of the chemical per se

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2. The duration of exposure

3. The quantity of the chemical

If a relatively large amount of a toxic chemical acts for a short period of time, the effects are acute, while relatively small amounts acting over long periods tend to produce chronic effects. Other more subtle effects have been noted, and cancer, modification of behavior, genetic effects, potentiation of the toxicity of other environmental compounds may also have to be investigated.

Clearly there is no one protocol by which to evaluate toxicity of every chemical. The following protocols are presented as guidelines only.

2.3 Physical and Chemical Properties

Basic information on physical and chemical properties are, of course, essential. These data are needed not only for analysis and monitoring, but to assess stability and determine whether and where a chemical is likely to be found in the environment. The following data can be easily gathered in a laboratory:

1. Chemical composition
2. Common name, if established
3. Chemical name (Chemical Abstracts, Wiswesser nomenclature)
4. Trade name
5. Structural formula
6. Melting point
7. Boiling point
8. Vapor pressure
9. Density or specific gravity
10. Solubility in water and in selected organic solvents and oils
11. Dissociation constants (pKa or pKb)
12. Physical state
13. Color
14. Odor
15. pH
16. Flashpoint
17. Viscosity

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Reactions and other characteristics of a chemical in relation to other compounds such as, water, air, and soil should include the following:

1. Oxidizing properties
2. Reducing properties
3. Corrosive hazard
4. Explosive characteristics
5. Hydrolysis rate
6. Photochemistry

2.3.1 Structure and Reactions

Elemental composition, structure, and formula weight may suffice to suggest various reaction a compound is capable of, but the chemistry of new compounds may be highly specialized, and predictive characteristics may not be apparent. In addition to the oxidative, reductive and hydrolysis reactions, reactions of biological importance should also be considered; for example, alkylation, dealkylation, esterification, isomerization, and conjugation with animal and plant constituents may aid in the choice of future testing procedures. Rates and degree of completion of reactions also are useful; for example, the rate of dehydrohalogenation of organochlorine compounds at high pH could provide leads to relative persistence.

2.3.2 Physical Properties

Knowledge of physical properties assists not only in determination of purity, but more importantly, aids in assessment of the potential behavior in and flow through the environment. Physical properties are also useful to the toxicologist in the design of his studies.

2.3.3 Impurities

Impurities such as residues of reactants, residual solvent and congeners, and the products of side reactions must be identified. Many final commercial products are deliberate mixtures. The toxicologist must recognize the problems of impurities and mixtures. The recent experience of 2,4,5T having dioxin contamination is an example. This impurity later was shown to have an LD_{50} for

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guinea pigs of 1 µg/Kg. Chlorobenzofuran appears to be not only a likely impurity of the parent PCBs, but may also be produced in the intended use of the PCBs; indeed it may even be a metabolic transformation product.

2.4 Information on Manufacturing Process and Possible Losses

The following data on manufacture will be useful in the assessment of PCB substitutes:

1. Description of the basic manufacturing process
2. Purity of starting and intermediate materials
3. Description of quality controls
4. Composition of the technical product including the names and amounts of impurities
5. Annual production reports
6. Present and anticipated uses
7. Means of transportation to site of use
8. Disposal of waste of production
9. Disposal of "spent" material that may contain the chemical
10. Accidental losses likely to occur

2.4.1 Production, Use, Disposal

Knowledge of the production, use and disposal of a chemical will be extremely helpful, along with physical and chemical properties, to estimate exposure levels to specific target systems. These estimates then can be used to identify the control systems that might be instituted to minimize release to the environment. In general, releases associated with production are amenable to controls on manufacturers; releases associated with use are amenable controls on users. Voluntary control over releases during use (equivalent to the voluntary controls exercised by Monsanto with regard to production) warrant further investigation, because the use of a chemical is intimately related to its potential release to the environment. Releases associated with disposal are also related to production and use, but are most easily controlled at the municipal level.

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2.4.2 Production Specifics

Production is the first level at which a chemical is likely to be introduced to the environment (i.e., through emissions); it is also at this stage that human toxicological data may be first obtained, through occupational exposure. Records of health and exposure levels of employees as now required by the Occupational Health and Safety Administration will be of inestimable value in assessing health effects; the discovery of hemangiosarcoma in workers exposed to vinyl chloride is an example.

Data on production and production losses must be obtained from manufacturers. Inventory statistics and data on methods of transport to major clients will be essential in quantifying losses. All data should be expressed on the final product, i.e., commercial grade, since impurities may prove more harmful than the product itself. Data on the losses from production and transport processes are of critical importance. Much of these data are company confidential and allowances will be necessary to protect confidentiality.

2.4.3 Uses

By far the most important information needed to estimate the exposure of a target population is a knowledge of the uses of a chemical. The first step in understanding how chemicals get to the environment would be to classify the uses into two categories: (1) contained uses, and (2) dispersive uses.

In general those uses designated as contained will not introduce large quantities of chemicals to the environment. However, experience with PCBs has shown that accidents, when they occur, frequently result in massive spills. Information on possible methods and amounts of release during normal contained usage should be carefully considered. The ultimate air route of dispersal of PCBs was never considered a serious threat, though it now appears this may be the major route of dispersal.

The use of consumer products containing toxic materials can result in significant direct exposure as well as affect the disposal pattern of these materials.

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2.4.4 Disposal

The disposal of chemicals in contained uses is, of course, a major concern, especially with persistent materials such as PCBs. Labelling and refund incentives may be necessary in order to get "spent" materials into the hands of persons knowledgeable in proper disposal techniques. The flow of discarded consumer products, however, presents a much more serious threat. Lack of ability to control this type disposal is obvious.

For products having a short life, disposal rates are approximately equal to production rates. For products with a longer life and rapidly growing consumption rate, the rate of disposal will be smaller than the rate of production and may be estimated from the service life of the product and from production records.

2.5 Environmental Rate - Chemodynamics, Environmental Alteration, and Bioaccumulation

2.5.1 Outline

The following outline lists the type of information needed to investigate adequately the toxicological consequence of introduction of a new chemical such as a PCB substitute. It is not meant to be conclusive but is only intended as a guideline. These data will assist the toxicologist in relating the adverse effect levels in animals to appropriate exposure levels for humans.

I. Movement and fate in water

- A) Dissipation rate in distilled water
  1. hydrolysis rate at acid, basic, and neutral pH
  2. photodegradation
- B) Degradation in water containing suspended solids
- C) Degradation in bottom sediments
- D) Rate and extent of movement in flowing water — chemical analysis of water downstream
- E) Bioaccumulation in aquatic microorganisms

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II. Movement and fate in soil

A) Soil metabolism studies — aerobic and anaerobic

B) Soil persistence studies

C) Leaching studies

III. Movement into and fate in air

A) Volatilization from water, soil and normal use

B) Photodegradation

IV. Fish uptake — in flowing water until plateau is reached and clearing in clean water

V. Biodegradability under sewage treatment conditions

2.5.2 Behavior in Aquatic Environment

The major factors contributing to the partition of a chemical into the aquatic environment are its solubility and latent heat of solution. Because so many organic compounds are hydrophobic, exact solubilities are difficult to obtain. Many of these compounds tend to accumulate at the air/water interface and to form clusters of varying particle size. Temperature, pH, salt content, and other variables affect solubility.

Microbial, photochemical and chemical transformations in aquatic systems play an important role in the ultimate fate of chemicals. Bioaccumulation occurs through:

1.) Direct, active ("intended") transport into an organism's system
2.) Active transport, where the compound is mistaken for one with similar properties (e.g., arsenic being taken up in place of phosphorus)
3.) Passive complex formation, with ligands in the organism
4.) Solubility equilibrium between fat (in the organism) and water

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The importance of item #4 can be appreciated by observation of the PCBs data showing that bioaccumulations exceeding 100,000 times the ambient level are reached in some microorganisms that are the primary food source of fish.

2.5.3 Behavior in Soil

The major processes affecting the behavior of chemicals in soils are adsorption and leaching-diffusion, both of which are influenced by temperature and moisture. Another process that affects transport of a chemical in soil is the chemical's movement with water. Although downward movement is most common, lateral and even upward movement are sometimes significant. The upward movement, which often is the result of evaporation at the surface, is effective in removing chemicals from the root zone, thus preventing possible movement into the food chain.

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15. Supplementary Notes

EPA Project Officer - Tom Kopp

16. Abstracts

This document presents the current state of knowledge about the production, usage and distribution of polychlorinated biphenyls (PCBs) in the United States. The information presented is derived from detailed studies on the production and first tier user industries, the past and present generation and disposition of PCB-containing wastes, environmental transport and cumulative loads, potential alternatives to PCBs usage, inadvertent losses to and potential formation in the environment, and current regulatory authorities for PCBs control. These results indicated that, although PCBs content of industrial wastes can be reduced through various approaches (treatment, substitution, etc.), there exists a potentially severe future hazard in the form of large amounts of PCBs currently contained in land disposal sites. Further definition of this and other aspects of the PCBs problem, and determination of ways to minimize the hazard, are recommended.

17. Key Words and Document Analysis. 17a. Descriptors

PCBs Properties
PCBs Manufacture
PCBs Users
PCBs Wastewater Treatment
PCBs Production & Distribution
PCBs Substitutes
PCBs Environmental Loads
PCBs Environmental Transport Model
Regulatory Actions on PCBs
Polychlorinated Biphenyls (PCBs)
Polychlorinated Terphenyls (PCTs)

17b. Identifiers/Open-Ended Terms

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Environmental Health Criteria 2

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NOTE TO READERS OF THE CRITERIA DOCUMENTS

While every effort has been made to present information in the criteria documents as accurately as possible without unduly delaying their publication, mistakes might have occurred and are likely to occur in the future. In the interest of all users of the environmental health criteria documents, readers are kindly requested to communicate any errors found to the Division of Environmental Health, World Health Organization, Geneva, Switzerland, in order that they may be included in corrigenda which will appear in subsequent volumes.

In addition, experts in any particular field dealt with in the criteria documents are kindly requested to make available to the WHO Secretariat any important published information that may have inadvertently been omitted and which may change the evaluation of health risks from exposure to the environmental agent under examination, so that information may be considered in the event of updating and re-evaluating the conclusions contained in the criteria documents.

WHO TASK GROUP ON ENVIRONMENTAL HEALTH CRITERIA FOR POLYCHLORINATED BIPHENYLS AND TERPHENYLS

Copenhagen, 20–24 October 1975

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ENVIRONMENTAL HEALTH CRITERIA FOR POLYCHLORINATED BIPHENYLS AND TERPHENYLS

A WHO Task Group on Environmental Health Criteria for Polychlorinated Biphenyls (PCBs) and Terphenyls (PCTs) met in Copenhagen from 20-24 October 1975. Dr F. A. Bauhofer, Director of Health Services of the WHO Regional Office for Europe opened the meeting on behalf of the Director-General and the Director of the Regional Office for Europe. The Task Group reviewed and amended the second draft criteria document and made an evaluation of the health risks from exposure to these compounds.

The preparation of the first draft criteria document was based on national reviews of health effects research on polychlorinated biphenyls, received from the national focal points collaborating in the WHO Environmental Health Criteria Programme in Canada, the Federal Republic of Germany, Finland, France, Japan, the Netherlands, New Zealand, Sweden, the United Kingdom, and the USA. Dr J. C. Gage, London, England, prepared the first draft as well as the second draft criteria document which took into account the comments received from the national focal points in Canada, Czechoslovakia, the Federal Republic of Germany, France, Japan, New Zealand, Sweden, the United Kingdom, the USA, and the USSR; from the United Nations Industrial Development Organization (UNIDO), Vienna, the Food and Agriculture Organization of the United Nations (FAO) Rome, and from the United Nations Educational, Scientific and Cultural Organization (UNESCO) Paris; the Organization for Economic Co-operation and Development, Paris, and the Health Protection Directorate of the Commission of the European Communities, Luxembourg.

Comments were also received at the request of the Secretariat, from Dr K. Kojima, Japan, Dr D. S. May, United Kingdom, and Dr V. Zitko, Canada.

The collaboration of these national institutions, international organizations and individual experts is gratefully acknowledged. Without their assistance the document could not have been completed.

This document is based primarily on original publications listed in the reference section. In addition, some recent publications reviewing the environmental and health aspects of polychlorinated biphenyls were also used. These include reviews by the Commission of the European Communities (1974), the US Department of Health, Education and

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Welfare (1972), the International Agency for Research on Cancer (1974), the International Council for the Exploration of the Sea (1974), Jensen (1974), Kimbrough (1974), the National Swedish Environment Protection Board (1973), the Panel on Hazardous Trace Substances (1972), the USDA/USDC/EPA/FDA/USDA (1972), and a WHO working group (1973).

Details about the WHO Environmental Health Criteria Programme including the definition of some terms frequently used in the document may be found in the general introduction to the Environmental Health Criteria Programme published together with the Environmental Health Criteria Document on mercury (Environmental Health Criteria 1, Geneva World Health Organization, 1976).

1. SUMMARY AND RECOMMENDATIONS FOR FURTHER RESEARCH

1.1 Introductory Note

The commercial production of the polychlorinated biphenyls (PCBs) began in 1930, and during the 1930s cases of poisoning were reported among men engaged in their manufacture. The nature of this occupational disease was characterized by a skin affliction with acneiform eruptions; occasionally the liver was involved, in some cases with fatal consequences. Subsequent safety precautions appear largely to have prevented further outbreaks of this disease in connection with the manufacture of PCBs, but from 1953 onwards, cases have been reported in Japanese factories manufacturing condensers.

The distribution of PCBs in the environment was not recognized until Jensen started an investigation in 1964 to ascertain the origins of unknown peaks observed during the gas–liquid chromatographic separation of organochlorine pesticides from wild-life samples. In 1966, he and his colleagues succeeded in attributing these to the presence of PCBs. Since that time, investigations in many parts of the world have revealed the widespread distribution of PCBs in environmental samples.

The serious outbreaks of poisoning in man and in domestic animals from the ingestion of food accidentally contaminated with PCBs have stimulated investigations into the toxic effects of PCBs on animals and on nutritional food chains. This has resulted in limitation of the commercial exploitation of PCBs and polychlorinated terphenyls (PCTs), and in regulations to limit the residues in human and animal food.

The environmental impact of the PCBs and PCTs has been the subject of several reviews, and has been discussed at a number of regional and international meetings. The relevant publications are mentioned in the previous section.

1.2 Summary

1.2.1 Composition and analytical problems

The commercial production of PCBs and PCTs by the direct chlorination of biphenyl and terphenyl leads to a mixture of components with a range of chlorine contents, the mean percentage chlorine in the product being controlled to give the required technical properties. Most of these components have been separated by gas–liquid chromatography, and the PCBs in the mixtures have been characterized after synthesis of the

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components by unequivocal routes. Techniques are available to analyse environmental samples for PCBs and PCTs, and experience has shown that interlaboratory collaborative studies are necessary to establish competence to determine residues below the 1 mg/kg level.

The commercial PCB mixtures contain various quantities of impurities, among which chlorinated dibenzofurans and chlorinated naphthalenes have been identified.

1.2.2 Sources and pathways in the environment

The estimated cumulative world production of PCBs since 1930 is of the order of 1 million tonnes. Of this, more than one-half has entered dumps and landfills, where it is likely to be stable and released only very slowly. Much of the remainder has entered the environment by the disposal of industrial fluids into rivers and coastal waters, by leakage from nonenclosed systems, or by volatilization into the atmosphere from incineration of PCB-containing material at dumps. The ultimate reservoirs of PCBs and PCTs that enter the environment are mainly sediments of rivers and coastal waters. PCBs and PCTs are stable in the environment, but a small proportion is transformed by biological action and possibly by photolysis.

1.2.3 Concentration in the environment

Measured concentrations of PCBs in air range from 50 ng/m^3 to less than 1 ng/m^3. Nonpolluted fresh waters should contain less than 0.5 ng of PCBs per litre compared with 50 ng per litre in moderately polluted rivers and estuaries, and 500 ng per litre in highly polluted rivers. The concentration in living organisms depends upon the extent of local pollution, the amount of fat in the tissues, and the trophic stage of the organism in food chains. Highest tissue levels were found in marine ecosystems with very high values in top predators from polluted areas, though most of the fish caught for human consumption contains PCBs at levels of less than 0.1 mg/kg in muscle tissue. There is no information available on the environmental distribution of PCTs.

1.2.4 Metabolism

PCBs are well absorbed by mammals through the gastrointestinal tract, lungs, and skin. They are stored mainly in adipose tissue and there is some placental transfer. Excretion in mammals is mainly through faeces, where the PCBs appear as phenolic metabolites; they appear unchanged in human milk. In birds, there is a considerable excretion in eggs. The rate of excretion in faeces is dependent on the rate of metabolism and this is much influenced by the number and orientation of the chlorine substituents. As environmental PCBs pass up biological food chains, there is a progressive loss of the lower chlorinated components owing to selective biotransformation, and only traces of PCBs containing less than five chlorine atoms per molecule are found in human fat.

The smaller amount of information available concerning the PCTs indicates that they also are absorbed from the gastrointestinal tract and undergo selective biotransformation, but that the concentration in fat in relation to that in other tissues appears to be less than is observed with the PCBs.

1.2.5 The extent of human exposure

Surveys on human adipose tissue in several countries have shown that most samples contain levels of PCBs in the region of 1 mg/kg or less, although higher values have been reported from some countries. Much higher values, up to 700 mg/kg, have been found in fat from men occupationally exposed. Several national surveys give PCB concentrations in the blood in the region of 0.3 µg/100 ml but levels approaching 200 µg/100 ml have been measured in men occupationally exposed, and these may be associated with skin lesions. Most surveys on human milk have shown PCB concentrations in the region of 0.02 mg/litre, although concentrations up to 0.1 mg/litre have been recorded. Results from the very few investigations on PCT concentrations in fat and blood suggest that these may be equal to those of PCBs.

An estimate of the total daily intake of PCBs in air, water, and diet by individuals not occupationally exposed indicates that this falls within the range of 5–100 µg, which may be supplemented by unknown amounts from nondietary sources. This estimate has some support from measurements of concentrations in human milk.

1.2.6 Experimental studies on the effects of PCBs and PCTs

Most of the studies on the toxicity of PCBs have been performed with the commercial mixtures. The PCBs are of low acute toxicity but the effects are cumulative with prolonged administration; in mammals, liver enlargement is observed that may progress to liver damage. Nonmetastasizing neoplastic liver nodules have been produced in rats and mice, some of which were classified as hepatocellular carcinomas on the basis of histological criteria in one study in rats and one study in mice.

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The monkey is much more sensitive to PCBs than the rat, showing effects similar to those seen in human Yusho patients (See section 8, p 65) with a similar order of exposure. Low dose effects on fertility have been seen in both the monkey and the mink, a species that is also relatively sensitive to PCBs.

Other effects of PCBs include porphyria, immunosuppression, and interference with steroid metabolism; some of these may be attributable to the increase in microsomal enzyme activity associated with liver enlargement. Some of the toxic effects can be attributed to impurities in the commercial products.

The toxicity of PCBs to fish is not high by comparison with that of some pesticides, but some aquatic invertebrates are more sensitive. There is little information on the toxicity of the PCTs.

1.2.7 Clinical studies of the effects of PCBs in man

Information on the effects of PCBs in man has been obtained from a large-scale incident in Japan (Yusho), in which over 1000 individuals showed signs of poisoning from the ingestion of rice oil contaminated with PCBs from a heat exchanger liquid. The most striking effects were hypersecretion in the eyes, pigmentation and acneiform eruptions of the skin, and disturbances of the respiratory system. Babies born to Yusho mothers were of less than normal size and initially showed skin pigmentation. Over a six-year period, the effects on the skin diminished very gradually, but the nonspecific symptoms tended to become somewhat more prominent. The smallest dose of PCBs calculated to produce an effect was approximately 0.5 g over about 120 days, but as the rice oil contained chlorinated dibenzofurans at a concentration of 5 mg/kg of rice oil in addition to PCBs at 2000–3000 mg/kg it is not certain that the symptoms were due solely to PCBs.

1.2.8 Dose–effect relationships

Experimental studies on the dose–effect relationship have shown that no effects on growth, and reproduction are seen in rats receiving PCB levels of 1 mg/kg body weight per day; there may be liver enlargement and a reversible induction of microsome enzyme activity at a level of 1 mg/kg/day but not at 0.1 mg/kg/day. Effects on reproduction are seen in the monkey with PCB levels of about 0.12 mg/kg/day. Symptoms were reported in some Yusho patients ingesting less than 0.1 mg/kg/day.

1.3 Recommendations for Further Research

1.3.1 Analytical methods

Collaborative intercalibration studies on the determination of PCBs, PCTs, and chlorinated dibenzofurans should be established between all laboratories engaged in determining these compounds in environmental samples, and adequate standards should be made available for individual chlorinated biphenyls and dibenzofurans.

Improved analytical techniques, including those involving capillary gas–liquid chromatography and mass spectroscopy, should be developed for the determination of PCBs, PCTs, polybrominated biphenyls, polychlorinated dibenzofurans, and naphthalenes, and their metabolites and degradation products.

1.3.2 Environmental pollution

The content of chlorinated dibenzofurans should be studied in a range of commercial PCB mixtures, and in used PCBs from existing or newly designed heat exchangers, capacitors, and hydraulic transmissions. The possibility of the formation of chlorinated dibenzofurans from PCBs in cooking oils before and after use and in other foods during storage or heating requires investigation.

The current production, use patterns, and methods of disposal of PCBs should be carefully examined to gain information on the impact of PCBs on the environment at the present time. The rate of leaching of PCBs from waste dumps and landfills should be studied, and methods of incineration should be investigated to ascertain which of the components survive inefficient combustion, and whether chlorinated dibenzofurans or other compounds are released into the atmosphere.

Information is required on the metabolism and environmental fate of the chlorinated dibenzofurans.

1.3.3 Effects on man

The intake of PCBs and PCTs from all sources by typical populations should be studied, and an attempt should be made to trace the sources of PCBs and PCTs in those items of the diet that make the greatest contribution to the daily intake. Further measurements are required on levels in human body fat, blood, and milk, and an attempt should be made to relate these levels to the daily intake.

Clinical and epidemiological studies are required on individuals

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ed to relatively high concentrations of PCBs and PCTs, either ationally or by virtue of the nature of their diet, and their health should be correlated with exposure and tissue levels.

Experimental studies

rther toxicological and metabolic studies are required on individual ilorinated biphenyls, dibenzofurans, naphthalenes, and other ities occurring in commercial products, on a variety of species ing primates, in order to assess the nature of the toxic effects, the esponse relationship, and the threshold of toxic effects. Such gations should be extended to include dermal and inhalation ire.

rcinogenic and cocarcinogenic studies should be undertaken to y the components in commercial PCBs responsible for neoplastic

PCB substitutes

ire information should be made available on the production and tterns of PCTs, polybrominated biphenyls, and of other possible utes for PCBs, and when appropriate, these products should be ed to adequate toxicological investigations.

2. PROPERTIES AND ANALYTICAL METHODS

2.1 Chemical Composition

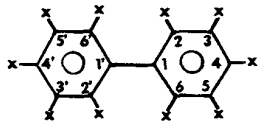
PCBs form a class of chlorinated hydrocarbons and are manu- l commercially by the progressive chlorination of biphenyl in the : of a suitable catalyst. They are known by a variety of trade Aroclor (USA), Phenochlor (France), Clophen (Federal Republic many), Kanechlor (Japan), Fenchlor (Italy), and Sovol (USSR). alue for industrial applications depends upon their chemical s, resistance to heat, non-flammability, low vapour pressure larly with the higher chlorinated compounds), and high dielectric t. There are many different trade names for mixtures of PCBs er compounds.

vidual manufacturers have their own system of identification for oducts. In the Aroclor series, a four digit code is used; biphenyls are generally indicated by 12 in the first two positions, while the last two numbers indicate the percentage by weight of chlorine in the mixture; thus Aroclor 1260 is a polychlorinated-biphenyl mixture containing 60% of chlorine. An exception to this generalization is Aroclor 1016 which is a distillation product of Aroclor 1242 containing only 1% of components with five or more chlorine atoms (Burse et al., 1974). With other commercial products the codes may indicate the approximate mean number of chlorine atoms in the components; thus Clophen A60, Phenochlor DP6, and Kanechlor 600 are biphenyls with an average of about six chlorine atoms per molecule (equivalent to 59.0% chlorine by weight).

In the Aroclor series, terphenyls are indicated by 54 in the first two places of the four digit code. In Japan, the PCTs are coded Kanechlor KC-C.

Individual PCBs have been synthesized for use as reference samples in the identification of gas–liquid chromatographic peaks, for toxicological investigations, and for studying their metabolic fate in living organisms, for which purpose they have been prepared labelled with carbon-14 (Hutzinger et al., 1971; Tas & de Vos, 1971; Webb & McCall, 1972; Moron, et al., 1972; Sundström & Wachtmeister, 1973; Jensen & Sundström, 1974).

The chlorination of biphenyl can lead to the replacement of 1–10 hydrogen atoms by chlorine; the conventional numbering of substituent positions is shown in the diagram. It has been calculated that 210 different



biphenyls of different chlorine content are theoretically possible, although Sissons & Welti (1971) have demonstrated that chlorine substituents in the 3,5- and 2,4,6-positions are not obtained by the direct chlorination of biphenyl. The proportions of PCBs with 1–9 chlorine substituents in the Aroclors are shown in Table 1.

There have been several investigations to identify individual PCBs in commercial products. Sissons & Welti (1971) separated the components of the Aroclors by column and gas–liquid chromatography, and characterized many of the peaks by high-resolution mass spectrometry and nuclear magnetic resonance, and by comparison with 40 synthesized

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Table 1. Approximate composition of Aroclors

ons	% of chlorine weight	Aroclor 1221[a]	1242[a]	1248[a]	1254[b]	1260[b]
	0	12.7				
	18.8	47.1	3			
	31.8	32.3	13	2		
	41.3		28	18		
	48.6		30	49	11	
	54.4		22	36	49	12
	59.0		4	4	34	38
	62.8				6	41
	66.0					8
	68.8					1

& Addison (1972).
on Hazardous Trace Substances (1972).

2. Polychlorinated biphenyls in Aroclors 1221–1254 (Webb & McCall, 1972)

etic	Aroclor					Reten-tion time*	Synthetic chloro-biphenyl	Aroclor				
yl	1221	1232	1242	1248	1254			1221	1232	1242	1248	1254
nyl	x [a] C'	x	x	x		60				x	x	
	x C	x	x	x		64				x	x	
	x D'					69				x	x	
	x C	x				69.5					x	x
			x			70	2,5,3',4'			x C'	x	
	x C	x	x C	x		70.5	2,3,6,2',5'					x C
	x	x	x			71	2,4,3',4'			x C'	x	
	x	x	x			72				x	x	
	x C	x	x	x		76	2,3,6,2',4'					x C
	x C	x	x C	x		82					x	
		x	x D	x		83	2,3,6,2',3'				x	x C
		x	x C	x		84					x	
	x	x	x C	x		86	2,4,5,2',5'				x	x C
	x C	x	x C			87	2,4,5,2',4'				x	x C
		x	x C'	x		98						x
		x	x C	x		99	2,4,5,2',3'				x	x C
		x	x C	x		101					x	x
		x	x C	x		104					x	x
			x	x		107	2,3,6,3',4'				x	x
			x C	x		115						x
			x	x		117					x	x
			x	x		119						x
				x		125	2,4,5,2',3',6'					x C
5'			x C	x	x C	126	2,4,5,3',4'				x	x C
5'			x C	x	x C	135						x
4'			x D	x		147						x
			x	x		148	2,4,5,2',4',5'					x C
5'			x	x	x C	149						x
			x	x		152						x
2',6'			x	x	x D	165						x
						178						x

re to p,p'–ODE at 190°C on 100' x 0.02" SCOT SE 30 column.
icates a GLC peak in this Aroclor at this retention time.
ns that the synthesic compound in the second column was confirmed by GLC and IR Aroclor. Because of the labour involved, most compounds were only confirmed in roclor. For example, biphenyl is probably present in 1232–1248 as well as 1221.
GLC data available.
thers also also present.

PCBs. Webb & McCall (1972) identified the gas–liquid chromatographic peaks with those of synthesized compounds by retention times and infrared spectrometry (Table 2). The most exhaustive study is that of Jensen & Sundström (1974). They recognized that conventional gas–liquid chromatography could not separate all the components, so they devised a preliminary fractionation on a charcoal column, which separated the component PCBs according to the number of chlorines in the 2,2',6 or 6' positions in the molecule (*o*-chlorines). They compared the gas–liquid chromatographic peaks with those of 90 synthesized PCBs, and were able to characterize and quantify 60 components of Clophens A50 and A60 (Table 3). Tables 2 and 3 show a considerable overlap between the components of Aroclor 1254 and Clophen A50.

2.2 Purity of Products

Commercial PCBs are *not sold on a composition specification*, but on their physical properties. Different batches may vary somewhat from the compositions shown in Tables 1–3. Impurities known to be present in commercial PCBs are chlorinated dibenzofurans and chlorinated naphthalenes (Vos et al., 1970; Bowes et al., 1975). Bowes et al. (1975) found chlorinated dibenzofurans at 0.8–2.0 mg/kg in samples of the Aroclor 1248–1260 series, but none in Aroclor 1016, and at levels of 8.4 mg/kg in Clophen A60 and 13.6 mg/kg in Phenoclor DP–6. Roach & Pomerantz (1974) found chlorinated dibenzofurans levels of 1 mg/kg and Nagayama et al. (1976) found 18 mg/kg in different batches of Kanechlor 400, but no chlorinated dibenzodioxins.

2.3 Determination of PCB Residues

Reviews have been published on methods used for the determination of organochlorine compounds including PCBs in environmental samples (Holden, 1973a, Panel on Hazardous Trace Substances, 1972). No two laboratories have identical methods, although all have features in common. The techniques appear to be those previously developed for the determination of organochlorine pesticides with appropriate modifications for the presence of PCBs, and the studies on PCBs sometimes form part of a wider programme for monitoring persistent organochlorine compounds in the environment. The major difficulties in the determination of PCBs are to separate them from interfering organochlorine pesticides, and to derive a single quantitative figure from a variable mixture of components.

Table 3. Percentages of polychlorinated biphenyls in Clophen A50 and A60 and in human fat (Jensen & Sundström, 1974)

Compound No.	Structure[a]	No. of ortho-chlorines	Relative retention time Apiezon L	Relative retention time SF 96	Percentage in Clophen A50	Percentage in Clophen A60	Percentage in Human tissue
1	2,5–2'5'	2	0.25	0.30	5.0		
2	2,4–2'5'	2	0.26	0.30	1.4		
3	2,3–2'6'	2	0.27	0.33	1.9		1.1
4	(2,–2',3',4')	2	0.30	0.43	1.2		0.66
5	(4–2',3'6')	2	0.32	0.43	2.1		0.56
6	2,5–2',3,6'	3	0.35	0.43	4.4[b]	2.9	1.2
7	2,3–2',3,6'	3	0.38	0.49	2.5[b]	0.28	0.48
8	3,4–2',5'	1	0.41	0.42	3.9		1.8
9		1 or 2	0.42		2.2[c]		2.0[c]
10	2,5–2',3',5'	2	0.45	0.49	2.2	1.1	1.2
11	2,3,6–2',3',6'	4	0.47	0.81	0.50	1.0[d]	
12	2,5–2',4',5'	2	0.48	0.50	7.0[b]	5.6	4.2
13	2,4–2',4',5'	2	0.51	0.51	1.8[b]	—[e]	1.9
14	2,3–2',4',5'	2	0.53	0.57	1.4[b]		
15	2,5–2',3',4'	2	0.53	0.58	5.4	1.4	2.3
16	2,3–2',3',4'	2	0.55	0.66	1.0		
17	3,4–2',3',6'	2	0.56	0.62	7.6[b]	2.9	4.7
18	2,3,5–2',3',6'	3	0.60	0.70	1.2	4.2	1.0
19	2,4,5–2',3',6'	3	0.64	0.73	2.0[b]	8.5[d]	0.13
20	2,5–2',3',5',6'	3	0.66	0.68	1.3	3.3	0.43
21	2,3–2',3',5',6'	3	0.70	0.74	0.5		0.05
22	2,3,4–2',3',6'	3	0.72	0.83	1.8	3.2	0.15
23		1 or 2	0.76		0.8[c]		
24	2,3,6–2',3',5',6'	4	0.77	0.91	0.09	0.96	
25	3,4–2',4',5'	1	0.79	0.74	5.0[b]	1.6	5.4
26	2,3,6–2',3'4',6'	4	0.84	0.96	0.05	0.37	
27	2,3,5–2',4',5'	2	0.86	0.86	0.90	2.9	2.7
28	3,4–2',3',4'	1	0.87	0.86	3.6		1.9
29	2,4,5–2',4',5'	2	0.90	0.86	4.2[b]	12.9[d]	21.5
30	2,3,4–2',3',5'	2	0.94	0.97	1.1	1.5	—[e]
31		1 or 2	0.96	0.93		—[e]	
32	2,3,4–2',4',5'	2	1.00	1.00	5.1	11.3[d]	14.0
33	2,3,5–2',3',5',6'	3	1.01	1.06	0.04	0.48	0.90
34		4	1.02		0.05[c]		
35		1 or 2	1.04	1.10	1.1[c]	2.0[c]	1.5[c]
36	2,4,5–2',3',5',6'	3	1.08	1.13	0.39	3.3	3.5

Table 3.—continued

Compound No.	Structure[a]	No. of ortho-chlorines	Relative retention time Apiezon L	Relative retention time SF 96	Percentage in Clophen A50	Percentage in Clophen A60	Percentage in Human tissue
37	2,3,4–2',3',4'	2	1.11	1.16	1.3	2.0	0.81
38	2,3,6–2',3',4',5'	3	1.13	1.29	0.33	3.7[d]	—[e]
39	2,4,5–2',3',4',6'	3	1.14	1.16	0.17	1.8	2.5
40	2,3,4–2',3',5',6'	3	1.19	1.32	0.27	2.1	1.3
41	2,3,5,6–2',3',5',6'	4	1.23	1.34	0.005	0.07	
42	2,3,4–2',3',4',6'	3	1.28	1.40	0.13	1.3	0.57
43	2,3,4,6–2',3',5',6'	4	1.34	1.44	0.007	0.09	
44	2,4,5–3',4',5'	1	1.41	1.19	0.47	1.0	0.49
45	2,3,6–2',3',4',5',6'	4	1.45	1.59	0.008	0.09	
46	2,3,4,6–2',3',4',6'	4	1.46	1.51	—[e]	0.03	
47	3,4–2',3',4',5'	1	1.55	1.37	0.81	1.5	2.0
48	2,3,5–2',3',4',5'	2	1.59	1.49	0.23	0.90	1.2
49	2,4,5–2',3',4',5'	2	1.71	1.56	0.38	7.6[d]	7.7
50	2,3,4–2',3',4',5'	2	1.88	1.82	0.72	4.1[d]	5.9
51	2,3,4,5–2',3',5',6'	3	1.94	1.99	0.08	0.74	0.77
52		1 or 2	2.02	1.96	0.23[c]	1.0[c]	—[e]
53	2,3,4,5–2',3',4',6'	3	2.07	2.05	0.06	0.44	0.94
54	2,4,5–2',3',4',5',6'	3	2.15	2.04	0.01	0.28	0.46
55	(2,3,5,6–2',3',4',5',6')	4	2.23				—[e]
56	2,3,4–2',3',4',5',6'	3	2.40	2.20	0.01	0.17	0.31
57	2,3,4,6–2',3',4',5',6'	4	2.45	2.56		—[e]	—[e]
58	3,4,5–2',3',4',5'	1	2.74	2.41	—[e]	—[e]	
59	2,3,4,5–2',3',4',5'	2	3.18	2.81	0.35	0.67	1.7
60	2,3,4,5,6–2',3',4',5',6'4	4	4.12				0.62
				Total	86.7%	99.4%	100.0%
		p,p'–DDE	0.52	0.58			
		p,p'–ODT	0.71	0.73			
		p,p'–DDT	0.90	0.97			

[a] Tentative structures are given in brackets.
[b] Component found present in Aroclor 1254 by Webb & McCall (1972).
[c] Figures calculated using responses of chlorobiphenyls with similar retention times in the same fraction from the charcoal column.
[d] Component found present in Phenoclor DP6 by Tas & Vos (1971).
[e] Present in trace amounts only.

2.3.1 Extraction of sample

Air

Particulate fallout from air has been trapped on 200 µm nylon net coated with silicone oil, and the PCBs then extracted with hexane (Södergren, 1972a). Separate determinations of particulate and vapour phase PCBs in air have been made by the passage of a large volume of air through a filter which was followed by an impinger containing hexane (Hasegawa et al., 1972b), or a polyurethane plug (Bidleman & Olney, 1974) or ceramic saddles coated with OV 17 silicone (Harvey & Steinhauer, 1974) to absorb the vapour.

Water

PCBs have been extracted from water by passing a sample through a filter of undecane and Carbowax 400 monostearate supported on Chromosorb W (Ahling & Jensen, 1970) or a porous plug of polyurethane coated with a suitable gas–liquid chromatographic stationary phase (Uthe et al., 1972), or Amberlite XAD–2 resin (Harvey, et al., 1973) followed by elution of the PCBs with a solvent. Anhoff & Josefsson (1975) have described a liquid–liquid extraction into cyclohexane.

Biological samples

Most analysts have used standard methods developed for organochlorine pesticides, in which the PCBs are extracted together with the fat; the sample is ground with anhydrous sodium sulphate and extracted with petroleum ether or hexane. Porter et al. (1970) studied the optimal conditions for this procedure. A dehydrating solvent may be included to facilitate the breakdown of cell structures; ethanol (Norén & Westöö,

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