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NERC/RTP POSITION PAPER

ON

POLYCHLORINATED BIPHENYLS

(PCBs)

U. S. ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

APRIL 1973

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NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

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PREFACE

This document was prepared by a Task Force convened under the direction of John F. Finklea, Director, National Environmental Research Center (NERC). The objective was to review and evaluate the current knowledge of polychlorinated biphenyls (PCBs) released into the environment as related to possible deleterious effects upon human health and welfare, with a view toward the preparation of a control strategy document, should such be required, in consonance with the provisions of the Clean Air Act as amended.

An extensive report prepared by an NIH Panel on Hazardous Trace Substances, chaired by Norton Nelson, served as a primary reference for the position paper. The report entitled "Polychlorinated Biphenyls - Environmental Impact," was published in Environmental Research, Vol. 5, No. 3, dated September 1972. Very recent data and information on PCB's in the marine environment were generously provided by Patrick L. Parker, Office of International Decade of Ocean Exploration (IDOE), NSF; and George R. Harvey, Woods Hole Oceanographic Institution.

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ENVIRONMENTAL PROTECTION AGENCY
National Environmental Research Center
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REPLY TO ATTN OF: James R. Smith, Chairman

DATE May 11, 1973

SUBJECT: PCBs Position Paper

TO: All Task Force Members (See Distribution)

Attached is a copy of our Position Paper. Copies are being sent to Dr. Wiser, ORM, for review. If you have further corrections or changes, we can incorporate them during the review of ORM. Please submit changes to me by 23 May.

Thank you for your cooperation.

James R. Smith
Chairman

Attachment

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SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. Background Summary

Polychlorinated biphenyls (PCBs) have been shown to be toxic; however, the degree of toxicity appears to vary significantly among compounds. Some are highly toxic and others appear to be non-toxic. Some of the chemicals have been found to be contaminated with chlorinated dibenzofurans and chlorinated dibenzodioxins -- both of which are known to be highly toxic. Severe cases of chloracne and acute liver disease have been associated with occupational or accidental exposure to nigh concentrations of PCBs -- either via inhalation, contact, or ingestion with food. Biological experiments have produced similar results. The most serious incident occurred in Japan in 1968 as a result of large-scale contamination of cooking oil. There is an increasing body of evidence that PCBs, which are now widely distributed in the environment, have had a deleterious effect upon certain biological species. Particular attention has been devoted to birds and fish.

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Polychlorinated biphenyls are a class of synthetic pollutants which have no known counterpart in the natural environment. The PCBs are manufactured by the chlorination of biphenyl with anhydrous chlorine using iron filings or ferric chloride as a catalyst. Two hundred and ten different chlorine-substituted biphenyls are possible, but the number observed in commercial formulations is much less. In their industrial applications, PCBs are relatively inert, stable chemicals with special dielectric properties. The higher-chlorinated species are nonflammable and have extremely low volatilities. Unfortunately, some of the characteristics which make PCBs so versatile in industrial

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applications also make them highly persistant in the environment.

PCBs were first produced commercially in 1929. They have since been used in many industrial products. The principal applications HAVE INCLUDED include: 1) non-flammable hydraulic and lubricating fluids, 2) heat-exchanger and dielectric-fluids, 3) plasticizers for plastics and coatings, 4) extenders for pesticides, and 5) ingredients for caulking compounds, adhesives, paint, printing inks, and carbonless duplicating paper.

The sole MAJOR producer of PCBs in the U. S., and probably the worlds largest producer, is the Monsanto Company. PCBs also are produced in Great Britian, France, Germany, the U. S. S. R., Spain, Italy, Czechoslovakia, and Japan. Cumulative sales in the U. S. since the introduction of PCBs, are estimated at approximately 5×10^5 tons. Estimates for foreign production are not available. Loss to the environment figures are practically non-existent. Rough estimates based upon applications suggest that approximately 20% of the cumulative PCB production is still in service. It is assumed that the remainder has been discharged into the environment by the various routes.

Monsanto Company has restricted the sale of Aroclor based upon consideration of possible contamination of food products, or their ability to control or monitor possible losses into the environment. Sales were to be restricted to confined systems entirely by 1972. No sales are made to food processors. Similar controls, to our knowledge have not been established by foreign manufacturers. Recommended procedure for thermal decomposition of PCBs is by burning in oil suspension with flame temperatures in excess of 1100°C - the products are CO_2, H_2O, and Hcl. Monsanto also has established special disposal facilities for its customers.

Available evidence indicates that PCBs with a chlorine content of 42% or less are degraded in the environment within a reasonably short period of time -- possibly by microbial action. Higher isomers degrade more slowly. Recent data indicate that the half-life of PCBs with chlorine concentrations greater than 50%, for example Aroclor 1254, is much greater than DDT. Non-biological degradation in the environment is expected to be slow.

Environmental transport models for PCBs have not been developed. Conclusions regarding their behavior are based largely upon the results of DDT research. With some modification models for DDT should be applicable to PCBs. The valadity of DDT measurements prior to 1969 is now being questioned due to the failure to correct for possible contamination by PCBs. The principal transfer routes for PCBs are: 1) aerial, 2) runoff, 3) sediments, 4) leaching from soil, or dumps, 5) uptake by organisms and plants, and 6) food transport. Little is known about specific pollutant dynamics. Recent data indicate that aerial transport is the most efficient route, although river runoff and dumping will contribute or more effectively to local contamination. Measurable concentrations of PCBs have been found in rainwater. Recent measurements in the oceans by the Woods Hole Oceanographic Institution reveal that PCBs are widely distributed. No significant horizonal gradients were observed, except in areas where dredge spoils were dumped or in the immediate vicinity of known sources of river runoff. This evidence indicates that aerial transport is dominant. Only very crude estimates of the annual losses of PCBs to the environment are available. These are: 1) 1.5 - 2.5 x 10^3 tons to the atmosphere, 2) 4-5 x 10^3 tons into fresh and

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coastal waters, 3) 6.8×10^4 tons into dumps and landfills, and 4) 10 tons into the soil as pesticide extenders.

Based upon our experience with DDT, and theoretical considerations, it has been postulated that PCBs would be found primarily on particulates in the atmosphere. Recent data do not support this conclusion. Atmospheric concentrations measured in the vapor phase at Bermuda in February 1973 ranged from 0.2 to 0.5 ng/m^3. No PCBs were found in the particulate analyses during the Bermuda study. However, the sampling technique used does not differentiate conclusively between particulate absorbed and vapor phase PCBs. PCBs have been found in particulate samples taken in urban areas. Similar conclusions were drawn regarding PCBs in the aquatic environment; i.e., that they would be found primarily in the sediment and absorbed on suspended matter. Recent measurements in the North Atlantic by the Woods Hole Oceanographic Institution do not fully support this conclusion. Concentrations reported in solution in the open Atlantic surface waters averaged 35 ppt (parts per trillion). (10^{12})

There are essentially no data available on the concentration of PCBs in the soil. It is expected that the amount would be small, except in the vicinity of dumps and land fills, if the estimates on the use of pesticide extenders are correct. This may not be the case if aerial transport proves to be dominant resulting in wide disposal of emissions from incomplete incineration.

Data on the concentration of PCBs in food are sparse. Measurable quantities have been found in fish, milk, and eggs. None have been found in fruits and vegetables, however, the search has not been extensive.

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Based upon the few available measurements made in fresh water, it is estimated that concentrations might range from 0.5 ppt in unpolluted rivers and lakes to 500 ppt in highly polluted water. It is postulated that little or no PCBs will be found in ground water, since it is expected that they would be absorbed on soil particles. Concentrations ranging from 10 to 100 ppt were reported in tap water in Japan.

The oceans and the soil are probably the primary sinks for PCBs in the environment. PCBs were measured in soil in the Baltimore area. The concentration ranged from 0 to 0.9 ppm. Reliable half-lifes for these mediums have not been determined. The persistance of PCBs in the environment should be comparable to DDT ppt.? Both DDT and PCBs are relatively non-polar and consequently will not be readily absorbed but also will not be washed out by polar molecules such as water. Some evidence suggests that the half-life of PCBs is that for DDT.

Certain marine species are known to concentrate PCBs by factors of 10^4 or greater over that found in the ambient waters. Uptake by phytoplankton has been found to be very rapid. Concentrations of 1-3 ppm have been measured in phytoplankton samples taken from the North Atlantic. The concentrations measured in zooplankton were less than in phytoplankton, and even less in fish. Maximum concentrations found in the ocean environment were measured in sea birds - approximately 100 ppm. The chromatogram peaks closely matched that of Aroclor 1254. No evidence of lower isomers (four or fewer chlorine atmos) were found.

Data were only recently obtained from the North Atlantic by the Woods Hole Oceanographic Institution (See Preface). These studies are not yet complete, and the results have not been published. A paper on

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the water analyses has been approved for publication in Science: G. R. Harvey, W. G. Steinhauer, J. M. Teal, Polychlorobiphenyls in North Atlantic Ocean Water, Science in Press (April or May). The results are very significant in that they fail to support important conclusions offered by other investigators concerning the transport and behavior of PCBs in the environment, as well as previously established concepts regarding food chain magnification.

Information regarding threshold values is limited. PCBs are toxic to some aquatic invertibrates at levels as low as 1 part per billion (ppb) in ambient water. As mentioned previously, they are known to be moderately toxic to fish. PCBs apparently are non-toxic to terrestrial insects, but act synergistically to increase the toxicity of several pesticides to insects. Experimental studies have shown that PCB concentrations of approximately 100 ppm adversely effect reproduction in birds and fish. There is strong suggestive evidence that adverse effects upon wild life populations, particularly birds and fish, may occur as a result of present levels of PCBs in the environment, although such effects are difficult to attribute solely to PCBs because the wild animals are exposed to other pollutants. During the Yusho incident in Japan, the minimum estimated toxic intake was 200 µg/kg/day. This is a much higher level than that to which the general population is exposed. FDA has established a maximum permissible level of 5 ppm in edible portions of fish, 2.5 ppm in separate milk fat (0.1 ppm in whole milk), and 0.2 0.5 ppm in animal feed. The American Conference of Governmental Industrial Hygienists has set a threshold limit value of 1 mg/m^3 for occupational exposure to vapors of Aroclor 1242 and Aroclor 1254, respectively and 0.5 m

Only very crude estimates of the mean daily intake for the general population are available. This would be highly variable depending upon the diet. The major intake would probably be from

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fish, milk, and eggs. Based upon available concentration data in air, water, and food, the mean daily intake for adults would probably be less than 100 µg/day.

Work on uptake, retention, and excretion of PCBs is incomplete. Very little work has been done on metabolism, and few metabolites have been identified precisely. There is circumstantial evidence that lower PCBs (tetrachloro and lower isomers) are metabolized very rapidly in the environment. Evidence suggest that differential metabolism is the primary mechanism in the environmental differentiation of isomers -- outweighing photolysis and mobility. Some higher PCBs appear to be metabolized by birds and mammals. The major storage tissue for PCBs is body fat - approximately 10-100 times the concentrations in other tissues. Mean levels of 1 ppm in human adispose tissue have been reported in the U. S., and Germany; respectively. However, in one study, 50% of the samples were negative.

Evidence regarding teratogenic, carcinogenic, and mutagenic effects of PCBs is incomplete. Little work has been done in these areas.

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B. CONCLUSIONS

Commercial production of PCBs began in 1929; however, these chemical compounds were not identified as environmental pollutants until 1966. Considerable research has been devoted to the toxicological properties of PCBs, but many important questions still remain unanswered. Critical research areas have been identified which will require several years for solution. In the meantime, it is important that action be taken to prevent further accumulation of toxic materials in the environment which may adversely effect the biota. Logical conclusions may be drawn from our present knowledge, which may serve as a basis for decisions regarding preliminary control actions. A number of conclusions expressed in the literature on PCBs are based upon extrapolation of our knowledge and experience regarding DDT, while others are well supported with reliable observations and experimental data. Recent data suggest that certain extrapolations based upon DDT properties and behavior may not be valid; therefore the risk of error must be accepted and weighed accordingly. The following conclusions represent the views of the members of the NERC/RTP Task Force on PCBs.

1) PCBs are toxic to humans and certain animal species; however the degree of toxicity varies depending apparently upon the chlorine content of the molecular structure.

2) PCBs are synthetic pollutants with no counterpart in the natural environment; therefore observed environmental concentrations represent solely the contribution from anthropogenic sources. The rate of release of PCBs into the environment has been significantly greater

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than the rate of degradation.

3) PCBs now are widely distributed in the environment. Measurable concentrations have been found in air, water, soil, and biota components.

4) Certain species of marine life may concentrate PCBs by a factor of 10^3 - 10^5. Further concentration may occur within the vertibrate food chain. Concentrations found in sea birds have been 10^7 - 10^8 times greater than those in ambient water.

5) The principal exposure route for humans is via food -- primarily fish in the diet. Intake via air and water are small in comparison, except in cases of contamination or occupational exposure.

6) Reliable threshold values for PCBs have not been determined. The population involved in the Yusho incident in Japan had an intake of 200 µg/kg/day or greater. PCBs are moderately toxic to some marine invertibrates at concentrations as low as 1 ppb in ambient water. Growth of phytoplankton is inhibited at levels of 10-100 ppb.

7) A reliable half-life for PCBs in the environment has not been determined; however, there is some evidence that it may be greater than for DDT.

8) Lower isomers (tetrachloro and lower) appear to be degraded rather rapidly in the environment. Some pentachloro and hexachloro isomers appear to be metabolized by birds and mammals, but the metabolites have not been identified.

9) Work on teratogenicity, mutagenicity, and carcinogenicity is incomplete. Conflicting results have been obtained.

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10) The long term health and environmental effects of PCBs have not been clearly established. A decrease in certain bird and fish populations has been associated with PCBs. (?) where is supporting data?

11) Present PCB concentrations in ambient air do not pose a direct threat to human health and welfare; however, the total concentration accumulated in the environment does pose a threat to some components of the ecosystem.

12) Prudent action should be taken to control the further release of toxic PCBs into the environment. Priority should be given to the prohibition of the use of toxic PCBs in non-confined systems whose primary disposal route probably would be through open-burning dumps or other inefficient or uncontrolled incineration processes.

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II. REVIEW OF SAMPLING AND MEASURING TECHNIQUES

A. Introduction

1. Structures

In a previous task force document on the PPOM the analysis of the large polynuclear compounds (4 to 7 rings) were discussed. These included the polynuclear aromatic hydrocarbons (or arenes), the aza arenes, the imino arenes, and arenes with one or more ring carbonyl groups. In this document we will discuss the analysis of the polychloro derivatives of the di- and tricyclic hydrocarbons: biphenyl, I, p-terphenyl, II, naphthalene, III, dibenzofuran, IV, and dibenzo-p-dioxin, V. (See Figure II-1). Two other terphenyls exist in addition to II; these are the o- and m- isomers. Most of the discussion will concern the polychlorobiphenyls (PCB).

Most of these compounds are marketed under a number of commercial trade names, e.g. Aroclor, Clophen and Phenoclor. The Aroclors from Monsanto Company are classified by a four digit number and consist of mixtures of polychlorinated biphenyls and terphenyls. The first two digits represent the hydrocarbon type, e.g. 12 are chlorinated biphenyls, 25 and 44 are blends of chlorinated biphenyls and terphenyls (75% and 60% biphenyl, respectively), and 54 are chlorinated terphenyls. The last 2 digits give the weight percent of chlorine, e.g. Aroclor 5460 is a chlorinated terphenyl containing 60% chlorine. Environmental PCB most often contains about 50% chlorine per molecule, that is from 4 to 8 chlorine atoms per molecule.

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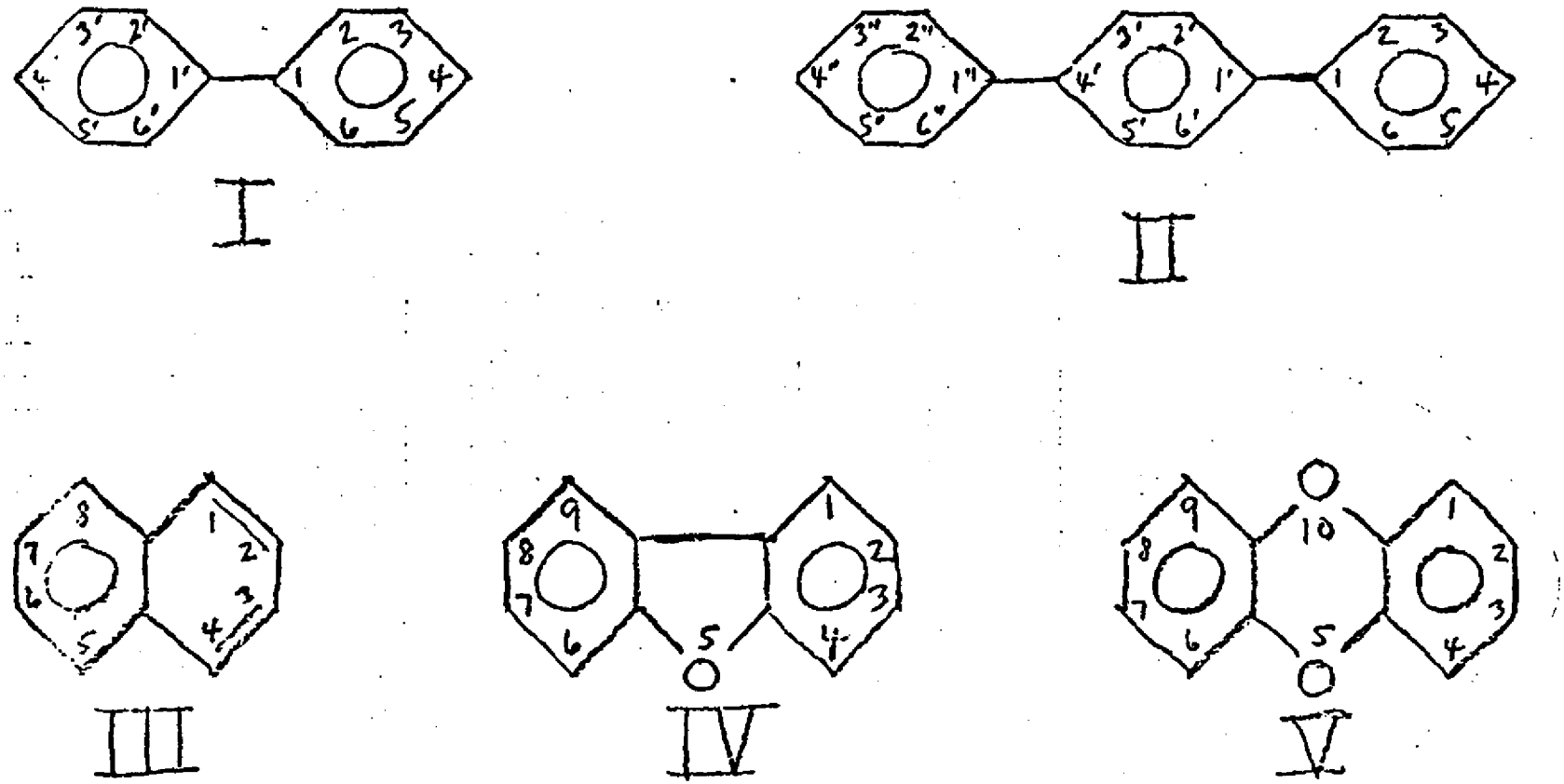

Figure II-1. Structure of Polychloro Derivatives of Di- and Tricyclic Hydrocarbons.

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An example of the polychloronaphthalenes available are the Halowaxes from Koppers Co. Inc., e.g. Halowax 1014 is a mixture of tetra-, penta- and hexachloronaphthalenes; Halowax 1051 is octachloronaphthalene; Halowax 1099 is a mixture of trichloro- and tetrachloronaphthalenes (1). The percent chlorine values for the different Halowax numbers are 1031 - 22%, 1000 - 26%, 1001 - 50%, 1099 - 52%, 1013 - 56%, 1014 - 62%, and 1051 - 70%.

2. Intercalibration and standardization

Since 1966 when the PCBs were found to be an environmental pollutant, (2) PCBs, along with DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane), have been reported to be the most abundant chlorinated aromatic pollutants in the global ecosystem (3).

It is evident that appropriate recommended methods are necessary to make it possible and meaningful to compare the PCB values obtained in widely separated laboratories. Expensive interlaboratory comparisons and standardization of methodology are going on constantly and much of this frenetic activity leaves an analyst in search of accuracy with a gnawing feeling of disquietude and a touch of dissatisfaction. It takes a committee quite a while to "standardize" a method and by that time it can become obsolescent. Because of the rapid evolution of methodology and instrumentation any method to be recommended for the use by laboratories new to the field, or for interlaboratory comparison, should be thoroughly evaluated in the laboratory and in the field so that its shortcomings and advantages are known. The most that such a method can be is a recommended tentative method.

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Some interlaboratory comparisons have been made for the PCB (4,5). Aroclor 1254 at the 1.1 and 2.1 ppm levels showed a percent recovery range of 63 to 95 (average 78) and 66 to 77 (average 73), respectively (4).

3. Contamination

Since the mixtures of PCBs, PCTs and PCNs (polychloronaphthalenes) are used as standard test mixtures, their contamination with polychloro derivatives of other ring systems becomes of some importance.

Polychlorodibenzofurans (PCDF) and PCN have been found in 2 commercial PCBs, Clophen A60 and Phenoclor DP6 (6). These mixtures were chromatographed on a florisil column, the 25% diethyl ether in hexane fraction evaporated to 1 ml, and this separated by GLC. From the fragmentation patterns obtained with mass spectrometric analysis the impurities were identified as tetra- and pentachlorodibenzofurans and hexa- and heptachloronaphthalenes. The upper limits of pentachlorodibenzofurans were estimated to be 5 ppm and 20 ppm in Clophen A60 and Phenoclor DP6, respectively. The gas chromatogram of the third fraction of Clophen A60 (Fig. II-2) and the mass spectrum of the pentachlorodibenzofuran (Fig. II-3) are shown. Thus, with the help of mass spectrometry about one nanogram of contaminant can be detected in a 100 µg sample. This means that the lower limit of detectability of contaminants without prior concentration is 10 ppm (7).

The physical and chemical properties of the PCB and PCN are similar (1, 8). Consequently, the PCN, in addition to some of the pesticides, interfere in the gas chromatographic analysis of PCB. Techniques should be

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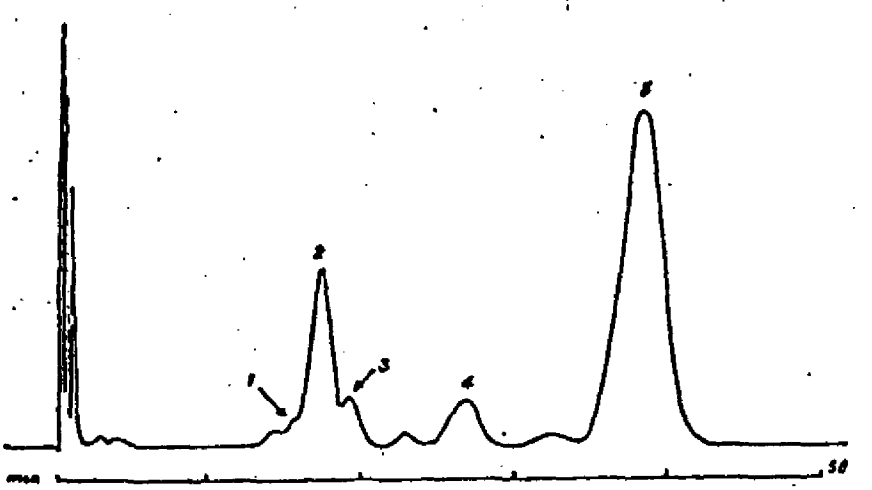

Figure II-2. Gas chromatogram of third fraction of Clophen A60 (showing pattern identical to that for third fraction of Phenoclor DP6). Data for peaks 1-5 are given in Table 2.

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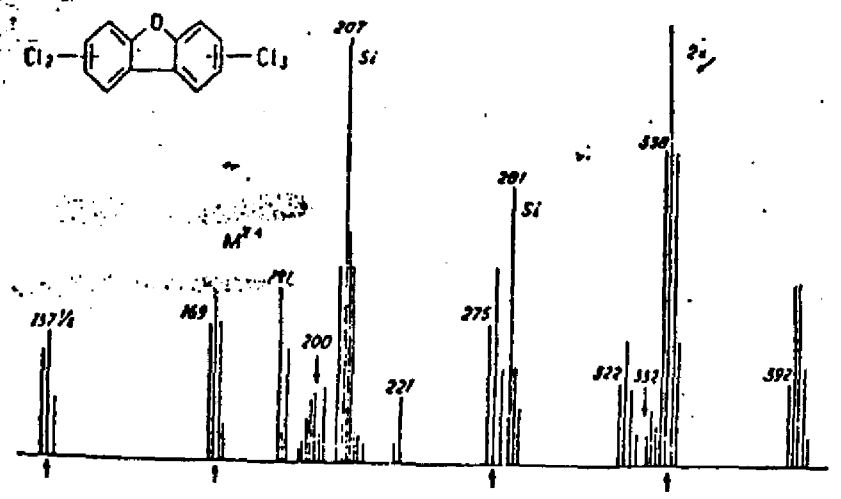

Figure II-3. Mass spectrum of pentachlorodibenzofuran (mass no. 338) obtained from third fractions of Clophen A60 and Phenoclor DP6 (Peak 4 in Fig. 1). The spectrum of heptachlorobiphenyl (mol wt 392) is also present.

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developed which would eliminate this interference. Preliminary studies indicate that PCN accompany PCB on silicic acid chromatography, but their presence can be detected from an absorption maximum at 306 nm, $A^{1\%}_{1cm}$ = 329 (9).

Another family of contaminants which have been found in commercial chloroaromatic compounds are the polychlorodibenzo-p-dioxins (PCDD) (10 - 13). In addition, 2,4,5-trichlorophenol and 2,4,5-trichlorophenoxyacetic acids have been found to be contaminated with PCDF and PCDD (13). Commercial chlorophenols were analyzed for trace contaminants by solution in aqueous alkali, extraction with petroleum ether, fractionation on an alumina column, and followed by examination by electron capture gas chromatography and combined gas chromatography - mass spectrometry (12). The presence of PCDD, PCDF and polychlorodiphenyl ethers (PCDE) was confirmed. The 2,3,78-tetrachlorodibenzo-p-dioxin was found in half the samples of 2,4,5-trichlorophenol. Hexa-, hepta-, and octachlorodibenzo-p-dioxins as well as a wide variety of PCDF and PCDE were present in most of the tetra and pentachlorophenols. In addition, the GC-MS data suggested that some of the chlorophenols contained methoxy and dimethoxy PCDF, and methoxy PCDE as well as hydroxy PCB.

4. Precursors

Some of the polychloro compounds are synthesized in the environment, or inadvertently as a byproduct in the preparation of some industrial chemical. The contamination described in the previous section is probably due to the latter type of synthesis.

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Polychlorophenols have been stated to be precursors of the PCDD (14). Some of the PCDD found in polychlorophenols and their sodium salt are shown in Table II-1. Some commercial grades of pentachlorophenol have been found to contain as high as 2500 ppm PCDD.

Since chloracne, liver involvement, etc., result from the handling 2,4,5-trichlorophenol, and this product is prepared by the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene, it has been concluded that byproducts which result during alkaline hydrolysis are the causative agents. These contaminants have been isolated and have been shown to be tetrachlorodibenzofuran and tetrachlorodibenzo-p-dioxin postulated to be formed by the type of reaction shown in Figure II-4.

Similarly the tetrachloro DD could be a contamininant in the herbicide 2,4,5-T(2,4,5-trichlorophenoxyacetic acid), since this compound is produced by the interaction of sodium monochloroacetate with 2,4,5-trichlorophenol.

5. Artifact Formation

One of the difficulties in many types of trace analyses is the problem of the formation of test substances during the analytical procedure. Thus, in searching for nitrosamines in cigarette smoke it has been found that substantial amounts can be synthesized from precursors in the test mixture during collection of the sample. An example of this frustrating problem is the synthesis of an octachlorodibenzo-p-dioxin on a gas chromatographic column during the separation of some isomeric nonachlorohydroxydiphenyl ethers (15), e.g.

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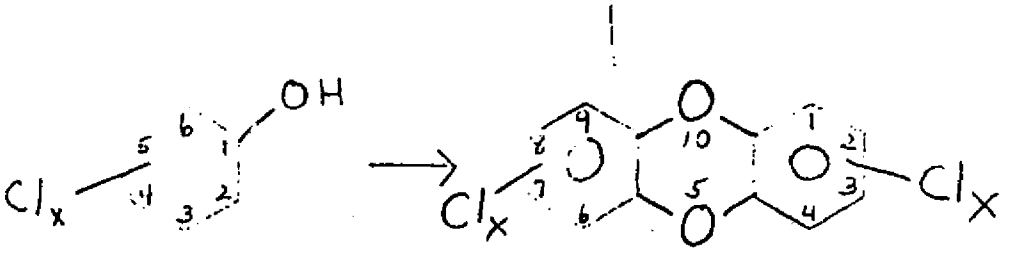
Table II-1.

Polychlorodibenzo(p)dioxins in Polychlorophenols

by Electron Capture Gas Chromatography (12)



Position of Chlorine Atoms

Sample No.	Phenol	PCDD	Found ppm
5	2,4,5-	2,7-	0.72
		2,3,7,8-	1.4
6	2,4,5-	1,3,6,8-	0.3
		2,3,7,8-	6.2
7	2,4,5-	Pentachloro	1.5
8	2,4,5-	None	-
9	2,4,5-	2,3,7,8-	0.07
10	2,4,6-	2,3,7-	93
		1,3,6,8-	49
11	2,3,4,6-	Hexachloro-	15
		Hexachloro-	14
		Heptachloro-	5.1
		Octachloro-	0.17
12	2,3,4,6-	Hexachloro-	4.1

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Table II-1 (Continued).

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Position of Chlorine Atoms

Sample No.	Phenol	PCDD	Found ppm
13	2,3,4,6-	None	-
14	Pentachloro (PC)	Hexachloro-	14
		Heptachloro-	5.4
		Heptachloro-	9.1
		Octachloro-	3.8
15	PC	Hexachloro-	20
		Heptachloro-	1.3
		Heptachloro-	10
		Octachloro-	3.3
16	PC	Hexachloro-	0.96
		Hexachloro-	38
		Heptachloro-	10
		Heptachloro-	39
		Octachloro-	15
17	PC	Hexachloro-	35
		Heptachloro-	23
18	PC	Hexachloro-	0.03
		Hexachloro-	0.14
19	PC	Hexachloro-	13
		Hexachloro-	12
		Heptachloro-	35
20	PC	Hexachloro-	0.91
		Heptachloro-	0.50
		Heptachloro-	1.6
		Octachloro-	5.3

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Table II-1 (Continued).

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Position of Chlorine Atoms

Sample No.	Phenol	PCDD	Found ppm
21	PC	Hexachloro-	15
		Heptachloro-	23
		Octachloro-	15

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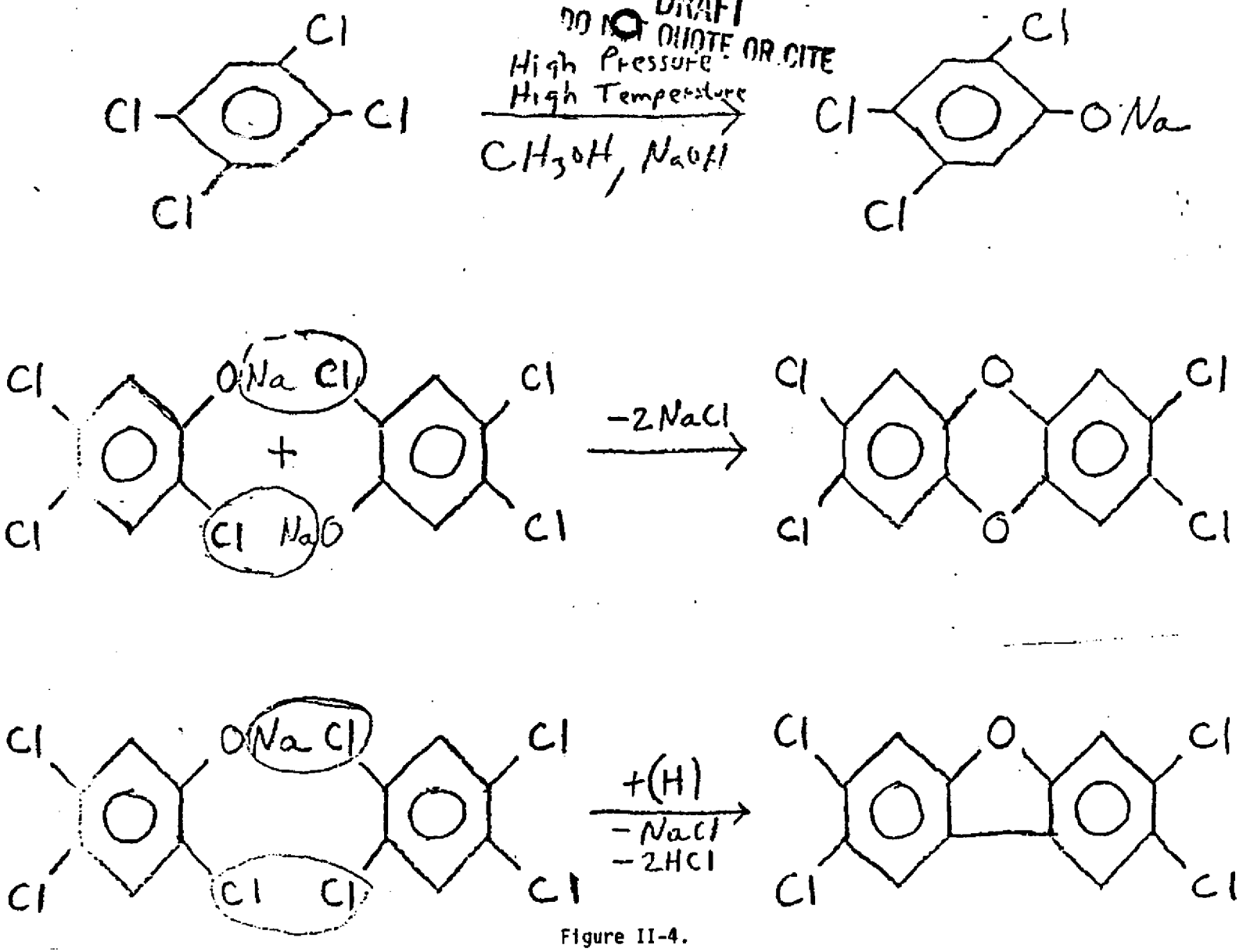

Figure II-4.

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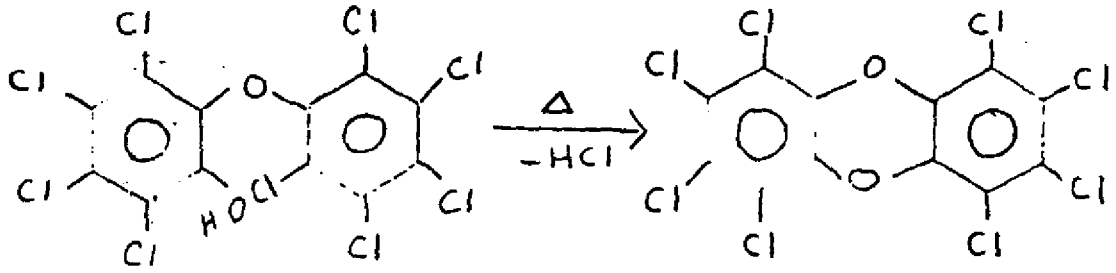

6. Stability

Although the polychloro polynuclear compounds are believed to be very stable in the environment, there are indications that they could be broken down or modified in an appropriate environment. The extremely high physiological activity of 2,3,7,8-tetrachlorodibenzo-p-dioxin would seem to denote a high order of chemical activity in living tissue.

Under mild conditions light can promote reactions in so-called unreactive halides. Both PCDD and PCDF are very unstable to light in the presence of organic substrates (16, 17)

B. General Methods

In the determination of the polychloro polynuclear compounds the following criteria are desirable - pure standards, a good calibration procedure, high collection efficiency (from air, water, etc.), complete extraction from the collected environmental mixture, no loss during cleanup, no degradation during the chromatographic steps, no artifact formation during the procedure, good overall recovery, reasonable sensitivity, no interferences, unequivocal characterization, as much simplification as possible, satisfactory intercalibration, capability of uninterrupted use in the automated or manual modes, and a high order of precision. With all this, all one can further ask for is accuracy.

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1. Standards

For reasonably accurate work, pure standards or mixtures with a known amount of test substance(s) are necessary. A few commercial sources are Aldrich Chemical Co., Analabs, Burdick and Jackson Lab., Chemical Procurement Labs., Eastman, K and K Lab., Monsanto Co., Pfalz and Bauer Chemicals, and Sapon Lab. For example, Analabs is a source of the following 99% pure standards - 50 PCB, 3 PCT, an octachloronaphthalene, 2 PCDD and an octachlorodibenzofuran.

Standards for PCBs (Aroclors 1221, 1232, 1242, 1248, 1254, 1260 and 1262) and PCNs (Halowaxs 1000, 1001, 1013, 1014, 1051, and 1099) are available from the Technical Services Division, Pesticides and Primate Laboratory, EPA, Perrine, Florida. Standards for Aroclors 1242, 1248, 1254, and 1260 are available from Pesticides Reference Standards Section, Office of Pesticides Program, EPA, Washington, D. C.

In addition, synthesis procedures for PCBs have been reported (18, 19). All the PCBs were homogeneous on silica gel thin layer chromato-gra gram plates developed with heptane and gave one peak when chromatographed on a 4% SE-30 column (18). The mass spectra of the compounds confirmed the molecular composition.

The Aroclor mixtures can be used as standards for measuring environmental mixtures containing PCB. A thorough analysis of the mixture must be performed beforehand. Aroclor 1254 has been used as such a standard, but the levels of PCB obtained have been much too high (20). Because of impurities in an Aroclor being used as a standard, quantitation based on that one Aroclor will be erroneous.

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However, semiquantitative measurements of PCB residues have been made using one peak of a commercial mixture as a standard (21). Quantitation has also been based on an average of 2 or more peaks.

The compositions of Aroclors 1242, 1254 and 1260 have been determined by elemental analysis, GC with a Coulson conductivity detector, and combined GC-MS (22). A procedure using these Aroclors is recommended for analyzing environmental samples containing more than one Aroclor mixture. In another GC procedure 6 Aroclor standards have been used so as to minimize the errors due to impurities (20). Chromatograms of six PCB standards were obtained for Aroclor 1232, 1242, 1248, 1254, 1260, and 1262. They were dissolved in hexane to concentrations of 2 ng/μl. A 4 μl injection placed peak heights on the linear portion of the standard curve for each Aroclor. Duplicate 4 μl injections were made. Total peak area for each Aroclor was determined by the cut and weigh method. Stock solutions of the Aroclors in isooctane are stable except when exposed to sunlight.

Another mixture which has been assayed by GC-MS to some extent is the French product, Phenochlor DP6 (19). Four of its major components are 2, 2', 4, 4', 5, 5' - hexachlorobiphenyl, the 2, 2', 3, 4, 4', 5' - isomer, and 2, 2, 3, 4, 4', 5, 5' - heptachlorobiphenyl and its 2, 2', 3, 3', 4, 4', 5 - isomer. This mixture could also be investigated as a standard.

Of course, more accurate quantitation will be achieved when pure individual PCB components become available.

A polybromobiphenyl mixture for standard use is Firemaster BP6 (hexabromobiphenyl) which gives 7 peaks with retention times of 0.50, 0.88, 1.09 (major peak), 1.44, 1.77, 1.94 and 2.82 (major peak) relative to decachlorobiphenyl on the OV-210 column (23).

The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin has been prepared from 2,4,5-trichlorophenol in pure form (10). Thirteen chlorinated dibenzo-p-dioxins containing from 1 to 8 chlorine atoms have been prepared for use as standards in the development of analytical methodology for the PCDD (24).

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Internal standards are also of value in checking recovery. There is a definite need for these standards since it is difficult to measure accurately the small volumes remaining after evaporations and the less than 10 ul volume injected into the gas chromatograph. This standard must have a retention time different from those of the PCBs and must be in a clear area of the chromatogram. Where much dilution takes place and the internal standard could be diluted to the point of invisibility, dilutions can be accomplished by means of a standard solution of the internal standard. In this way the peak of the internal standard is referred to the corresponding peak in the standard solution. DPDE (1,1-diphenyldichloroethene) has been used as an internal standard in residue analysis. A standard injection of a standard such as p, p'-DDE can indicate whether detector sensitivity has changed from when the response curve was calculated (20) and so a simple factor can be applied to the entire curve and all isomers quantitated as before.

2. Contamination

During the analysis for PCB and other polychloro polynuclear compounds, great care must be taken to avoid contamination of samples, since PCB may be present in a variety of products. PCBs of the 40% chlorine variety has been found in cardboard and in a wrapping plastic material. Glassware should be washed with chromic acid and liquid-chromatographic columns should be eluted with petroleum ether prior to use. The presence of aromatic hydrocarbons in pesticide-grade hexanes can affect the elution patterns of PCB and other chlorinated compounds from silicic acid columns (9). Several batches of silicic

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acid Silicar ^{R} (Mallinckrodt) were contaminated with 0.031 to 0.163 µg g of PCB expressed as Aroclor 1254. Hexane of satisfactory purity is difficult to obtain. It is reported to contain a significant amount of an impurity that has the same retention time as that of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Efforts to remove with fuming sulfuric acid, potassium permanganate or alkaline silver nitrate were fruitless. The only solution is the use of distilled batches of carefully selected hexane. The many usages of the PCB shows the wide extent of contamination possible (25).

3. Sampling

In sampling for PCB in air, water, soil and tissues different factors are involved. The collection efficiency and the physical state of the test substances are of importance in air analysis. The way the material is collected will depend on whether it is in the vapor and/or the particulate phase, the volume of air flowing through the samples per unit time, the temperature of the air, and the composition of the atmosphere in terms of its pollutants.

The solubilities of the PCB in water and their attraction to the particulate phase will determine whether water, aqueous particulate, mud, etc. are collected.

Sampling of air, water, soil and tissues will be discussed more fully in the appropriate sections.

4. Interfacing - Sampling to Separation

A cleanup procedure is necessary to concentrate the polychloro compounds and to eliminate all the interferences, if possible. One of the big problems has been that the PCB are extracted together with other hydrocarbons and their halo derivatives. Since many of the chloro compounds have retention times identical to the PCB on non-polar columns,

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their analysis presents a problem which is not completely soluble by gas chromatographic means alone. Accusations have been made that much of the data obtained in the past for the pesticides are unreliable because of this problem, and because of the lack of proper confirmatory techniques.

The use of the electron-capture detector in the analysis of the polychloro compounds has the advantage of high sensitivity and the requirement for small amounts of material for analysis. But, a vigorous cleanup procedure is necessary to prevent gross contamination of the detector by other chlorinated compounds present, and to remove interfering substances with the same retention times as the PCBs. No single cleanup procedure is adequate. Most of the cleanup methods used for this separation employ adsorption column chromatography and constitute a difficult and time-consuming step. Some of the problems associated with adsorption column cleanup methods are contamination of the adsorbent, involved procedures for adsorbent preparation, the large quantity of clean glassware required; and the errors that may be introduced by way of adsorptive loss of residues on glass, plastic surfaces, on the column, and from interfering substances present on the adsorbent or in the eluting solvent.

Separation prior to gas chromatography has been used by many researchers. Simpler chromatograms are obtained. Thin layer chromatography, reverse paper chromatography and column chromatography afford means of obtaining partial separations of chlorinated compounds from PCB and fractions can easily be obtained where only Aldrin, Heptachlor and p p' - DDE remain with the PCB. The former two show

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little interference with PCB bands, but p p' - DDE can emerge with the major PCB peaks using non-polar compounds. TLC has given this sort of separation using silica gel and alumina (26) as has column chromatography with alumina or silica gel (27), or Florisil (28). It is possible to carry out a separation leaving only Aldrin with the PCB (29). Column chromatography with silicic acid - celite and elution with petroleum ether is used. This type of separation is possible as long as the column is not overloaded and there is no trace of polar solvent in the sample. Double column systems have also been used, e.g. alumina partly deactivated with 5% water followed by silica gel.

Solvent partition methods also can be used prior to separation, e.g. acetonitrile or dimethylsulfoxide/hexane. The polychloro compounds can be extracted into hexane and then into dimethylsulfoxide or dimethylformamide, water is then added and they are re-extracted into hexane.

Another possible method is through chemical change of the test substances or of the interferences, and in so doing changing either their physical properties or retention time so they present no interference to the PCB. Thus, pesticides can be nitrated (30) in hopes that the PCB are unaltered while the DDT is essentially removed. Unfortunately some DDT derivative peaks emerge on the chromatogram and some of the lower chlorinated PCB are affected.

Alternatively, saponification with alcoholic potash leads to the dehydrochlorination of p p' DDT, p p' TDE, and Toxaphene with the derivative peaks appearing earlier in the chromatogram and the

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PCB reportedly unaffected. BHC is destroyed by this procedure. PCB can also be differentiated from DDT using carbon-skeleton chromatography.

Sulfuric acid can also be used as a cleanup agent (31). One modification involves shaking up the hexane extract with $H_2 SO_4$ (32). This treatment destroys dieldrin and organophosphate pesticides.

5. Separation

The standard method for analyzing the PCB fraction of an extract is by gas chromatography. We will first discuss the separation of the PCB from other interfering molecules. Because of their similar polarities and chemical properties the PCBs in a sample are carried through the usual pesticide extraction and screening procedures,and are frequently mistaken for DDT and analogs in routine monitoring. PCBs accompany chlorinated hydrocarbons in the usual extraction and cleanup techniques,and both groups must be separated before quantitation by gas chromatography. Column and thin layer chromatography are usually used for the separation. PCBs are eluted from Florisil columns with hexane, DDT and other pesticides with mixtures of ether and hexane (28). Other workers have shown that successful implementation of this method requires a preliminary examination of the elution behavior of the pesticides from Florisil (33). Column chromatography on silicic acid separates PCB from all common chlorinated hydrocarbon pesticides except p, p' - DDE (27),and under very carefully controlled conditions even from p, p' - DDE (29). DDE and PCB can be eluted on activated Florisil columns with n-hexane with dieldrin and endrin eluting with 10% diethyl ether in

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hexane (21). PCB can also be separated from the chlorinated pesticides by column chromatography on charcoal. The latter are eluted with 25% acetone in ethyl ether and PCB are subsequently recovered by elution with benzene. Column chromatography on alumina is used to separate PCB from PCDD (34).

The difficulty in most of these separations is the separation of PCB from p, p' - DDE. One way of canceling this problem is to oxidize p, p' - DDE to 4, 4' - dichlorobenzophenone without affecting the PCB (35, 36). Chromium trioxide was used as the oxidizing agent.

TLC on alumina with heptane as developing solvent has been used to separate PCB from the pesticides. The spots were extracted with methanol - hexane and analyzed by gas chromatography (37). Other TLC methods of this type include separations on silver - nitrate - coated alumina with 5% benzene in hexane, or hexane after CrO_3 oxidation of p, p' - DDE (35, 36), a two - dimensional technique (38), and reversed phase TLC (39).

Chromium trioxide has also been used to oxidize PCN in the presence of PCB and thus cancel this interference (40). Where both of these families exist together, or PCNs are found in the presence of the chlorinated hydrocarbon pesticides, this interference in GC analysis definitely exists (41). A silicic acid column chromatographic method has been used to separate PCN from the pesticides and permits GLC determination without interference (42).

Some PCDD have also been separated from the PCB with the help of alumina column chromatography (34) and alumina column chromatography (43). After isolation electron capture gas chromatography is used for analysis.

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For the separation of individual members of the PCB or other polychloro compounds gas chromatography has been the method of choice. Column temperatures have usually ranged around 180° to 200°. A wide variety of chromatography packing has been used, e.g. DC-200 on Chromport 30, DC-200 on Chromosorb W, 10% DC-200 on Gas-Chrom Q, SF-95, QF-1, 1% SE30 on Chrom Q, OV-1 silicone oil, Silicone Epikote on Diatomite CQ, 6% QF-1,and 4% SE-30 on Chromosorb W. One of the most frequently encountered is the silicone grease SE-30, often mixed with other material such as QF-1. An example of some of the separations obtained and the detector response is given in Table II-2 (44). The separation was accomplished on a glass column (6 ft x 4 mm) containing 4% SE-30 on acid washed Chromosorb W (100 - 120 mesh) operated at 200°.

Thin layer chromatography can also be used to separate the PCB (39). Kieselguhr G saturated with 8 vol. % liquid paraffin in petroleum ether is developed with acetonitrile - acetone - methanol - water (40: 18: 40: 2) saturated with liquid paraffin. The type of separation is shown in Table II-3. The reversed phase partition TLC system can be useful for the separation of the components of a PCB mixture and can be used in combination with GC for the study of the composition of PCB residues. Visualization of the TLC spots was accomplished by UV irradiation of the silver nitrate sprayed plate.

PCT are not eluted from GLC columns used for PCB. They can be determined by GLC on a 6 ft x 4 mm glass column, containing 3% OV-210 on Chromosorb WAW 60/80 and operated at 200° (45) or on a glass column (6' x 1/4") packed with 3% Dexsil 300 on 100 - 120 mesh Gas -

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Table II-2

Retention time and electron-capture detector response of chlorobiphenyls

Compound	Relative retention time (p,p'-DDE=1.00)	Relative response per ng ± standard deviation (p,p'-DDE=1.00)
4-chlorobiphenyl	0.17	0.0033±0.00005
2- "	0.11	0.0030±0.00004
3- "	0.14	0.0006±0.00001
4,4'-dichlorobiphenyl	0.30	0.0152±0.0002
3,3'- "	0.25	0.0155±0.0001
2,2'- "	0.15	0.0131±0.0001
3,4- "	0.28	0.0388±0.0002
2,4- "	0.19	0.0450±0.0004
2,6- "	0.16	0.0815±0.0049
2,4,4'-trichlorobiphenyl	0.39	0.298±0.010
2,4,6- "	0.24	0.276±0.006
2,2',4,4'-tetrachlorobiphenyl	0.51	0.206±0.003
3,3',4,4'- "	0.96	0.770±0.027
2,2',6,6'- "	0.33	0.0403±0.0016
3,3',5,5'- "	0.70	0.625±0.045
2,3,4,5- "	0.69	0.715±0.010
2,3,5,6- "	0.51	0.505±0.010
2,3,4,5,6-pentachlorobiphenyl	1.00	1.30±0.017
2,2',4,4',6,6'-hexachlorobiphenyl	0.78	0.545±0.029
3,3',4,4',5,5'- "	2.98	1.15±0.064
2,2',3,3',4,4',6,6'-octachlorobiphenyl	2.62	1.58±0.020
2,2',3,3',5,5',6,6'-octachlorobiphenyl	2.45	1.53±0.076
Decachlorobiphenyl	8.20	1.61±0.086
Aroclor 1254		0.910±0.008
Aroclor 1260		1.35±0.010

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Table II-3

Relationship between Spots Obtained by TLC and Peaks Obtained by GC of Phenochlor DP6

Spot No.	Corresponding Peak No.
1	13
2	11
3	6, 9, 12
4	7, 8, 10
5	2, 4, 5
6	3, 6
7	1, 3

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Chrom Q, operated at 310° (46).

PCDDs can be separated on a column of 2% OV-17 on Diatomite CQ or 1% Hi-Eff 8 BP on Gas Chrom 2 (10), or on a stainless steel column coated with Dexsil 300 and programmed from 150° to 215° with helium as carrier gas and flame ionization detection (11).

Examples of separations are shown for Aroclor 1260 (Figure II-5), Aroclor 1254 (Figure II-6), and for PCDD, PCDE and PCDF (Figure II-7) (12).

6. Analysis

Some of the methods worth improving, which are believed to be gaining wide acceptance (47), include procedures developed by FDA (48), Official Methods of Analysis, 1970 (49), Armour and Burke (29) and Porter et al (50).

The many unidentified compounds in PCB preparations complicate the quantitation of PCBs. Assay has been by total peak area (29) or area under one (21), two (51) or more (52, 53) peaks, or peak heights (53 - 56). A method based on the average electron-capture detector response to PCB containing one to seven chlorine atoms also has been described (20). But since position of substitution affects the response, it is no more accurate than the others.

The dissatisfaction with the accuracy obtained is evident from the many methods of quantitation being used. Some people estimate that the quantitation of PCB is accurate only within a factor of 2 (57), whereas others assert it is impossible at the moment to quantitate PCB with any degree of confidence (58).

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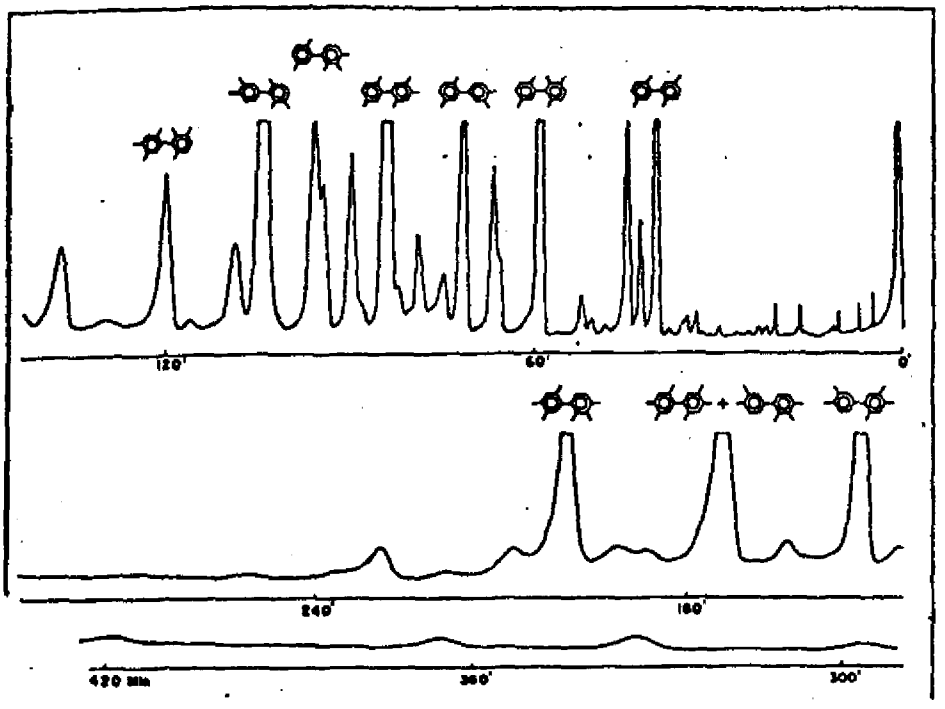

Figure II-5. Separation of Aroclor 1254 by capillary column-gas chromatography. Conditions: 50 ft. x 0.02 in. SCOT Apiezon-L column; 205°; He flow 2.5 ml/min; flame-ionisation detector. Structures of isomers responsible for major peaks are indicated (60).

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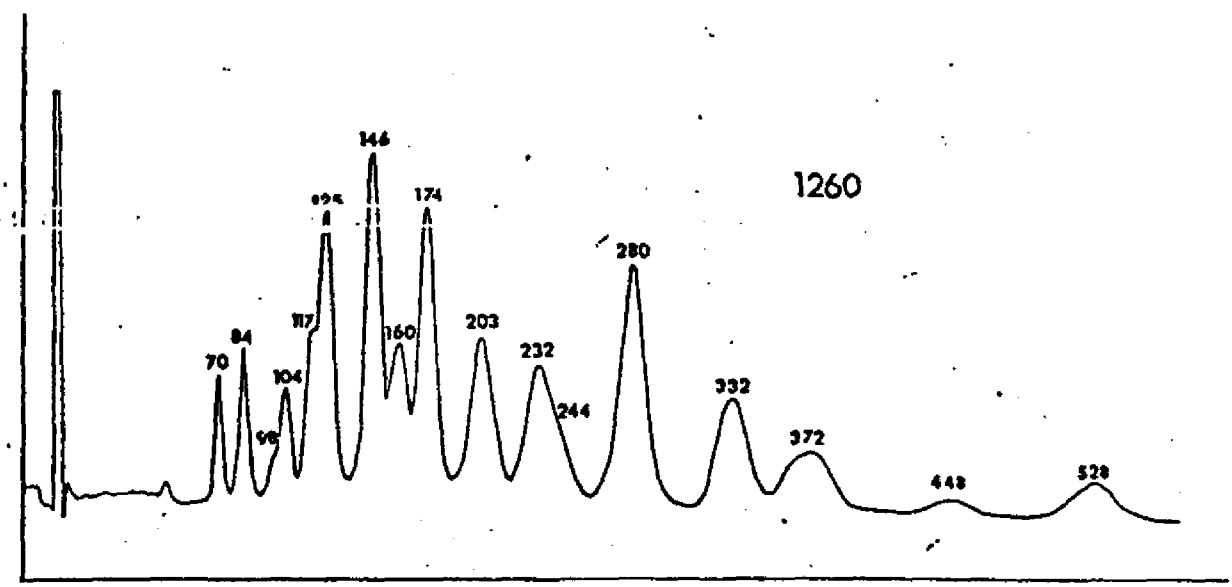

Figure II-6. EC chromatogram of Aroclor 1260 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100 (22).

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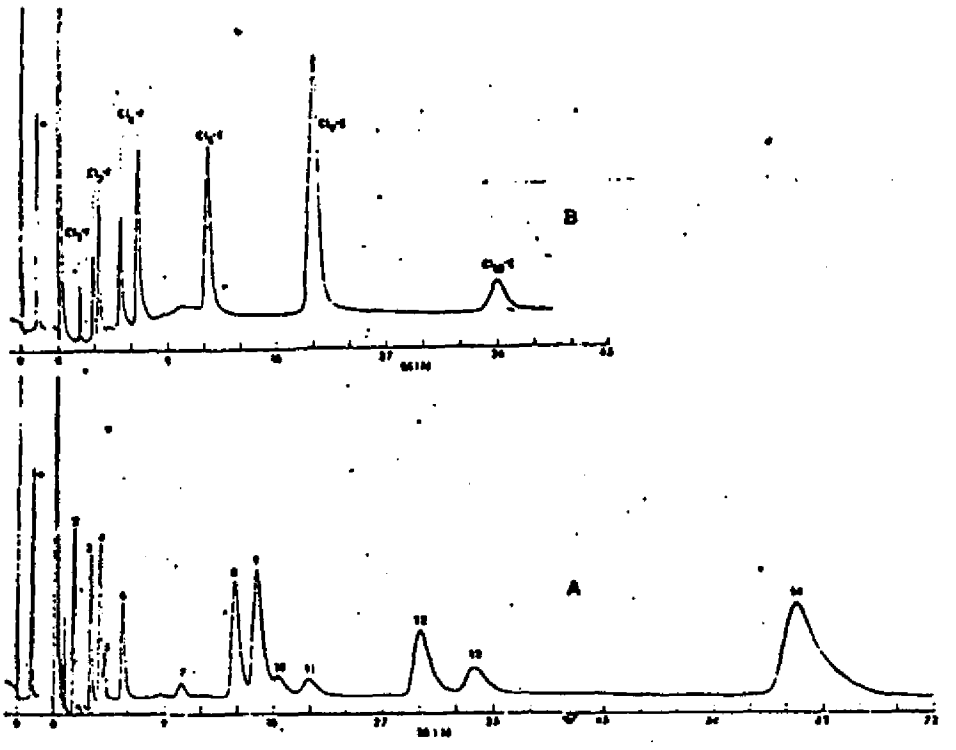

Figure II-7. A, Gas chromatogram of a mixture of chlorodibenzo-p-dioxins (Cl_n-D): (1) 2-Cl-D; (2) 2,7-Cl_2-D; (3) 2,3,7-Cl_3-D; (4) 1,3,6,8-Cl_4-D; (5) Cl_4-D isomer; (6) 2,3,7,8-CL_4-D; (7) Cl_5-D isomer; (8), (9), (10), and (11) Cl_6-D isomers; (12) and (13) Cl_7-D isomers; (14) Cl_8-D; a = aldrin standard. B, Gas chromatogram of a mixture of di-, tri, and tetrachlorodibenzofurans (Cl_n-F) (Cl_2-F, Cl_3-F, and Cl_4-F) and octa-, nona-, and decachlorodiphenyl ethers (Cl_n-E) (Cl_8-E, Cl_9-E, and Cl_{10}-E); a = aldrin standard.
EC-GLC conditions: 7' x 4 mm id glass coiled column packed with 3% XE-60 on 80-100 mesh Gas-Chrom Q; column temperature, 215°C; detector voltage, 80 v (tritium source); 1 x 10^{-9} AFS; nitrogen flow rate, 55 ml/min. Three µl containing 4-140 ng of each component was injected (12).

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--Quantitation of PCB from electron capture chromatograms is complicated because the EC detector responds differently to each PCB isomer (44, 59). The wide response is demonstrated in Table II-2. Quantitation by direct comparison of an unknown EC chromatogram with those of Aroclor standards is difficult because individual peaks in environmental samples are sometimes obscured by pesticide residues are completely missing, or have considerably different relative intensities.

The weight of PCB present in each GC peak of a given Aroclor can be calculated from two pieces of information: (1) the empirical formula of the compound represented by the peak, and (2) the absolute amount of chlorine represented by the peak. Combined GC - MS determines the first, and a GC equipped with an electrolytic conductivity detector can determine the second. The results are shown for Aroclor 1260 in Table II-4 and Figure II-5. The gas chromatograms of Aroclor 1254 and of a mixture of PCDD and PCDF are shown in Fig. II-6 (6D) and Fig. II-7 respectively (12).

PCT can be determined by GC on a 6 ft. x 4 mm glass column containing 3% OV-210 on Chromosorb WAW 60/80 and operated at 200° (7). Eight major peaks are obtained.

It is also possible that the PCB can be analyzed by pulsed source-time resolved phosporimetry, as has been done with the monohalobiphenyls, Table II-5(61). The limits of detection for the three 4-halobiphenyls are about 1 ng, for 2- and 4-chlorobiphenyls about 10 ng, and for 3-chlorobiphenyl about 10 μg. It also seems probable that time resolved phosphorimetry could be of value as a confirmation technique.

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Table II-4

Composition of Aroclor 1260 (22).

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
[98	3.8	3.5	] [d]
[104			5] 60%
			6] 40%
117	3.3	6.7	6
125	12.3	3.3	5] 15%
			6] 85%
146	14.1	3.6	6
160	4.9	2.2	6] 50%
			7] 50%
174	12.4	2.7	6
203	9.3	4.0	6] 10%
			7] 90%
[232			] [e]
[244	9.8	3.4	6] 10%
			7] 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

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Table II-5.

Phosphorescence Characteristics of Selected Halogenated Biphenyls (61)

Halogenated Biphenyl	Peak Phosphorescence Emission Wavelength,[a] nm	Phosphorescence Lifetime,[b] msec
2-Chlorobiphenyl	465	170.
3-Chlorobiphenyl	480	1300.
4-Chlorobiphenyl	477	570.
2-Bromobiphenyl	475	3.3
3-Bromobiphenyl	480	58.
4-Bromobiphenyl	480	17.
4,4'-Dibromobiphenyl	485	12.
2-Iodobiphenyl	490	3.0
4-Iodobiphenyl	480	3.2

[a]Solvent: ethyl alcohol.
[b]Relative errors in lifetimes are less than 10%.

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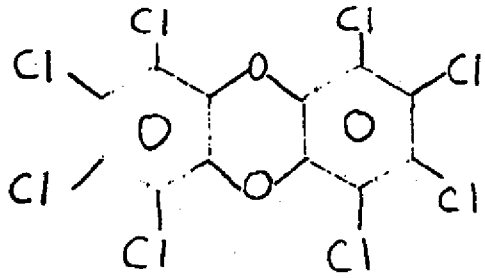
To avoid difficulties in quantitation, the PCB in a sample can be converted to decachlorobiphenyl and the EC signal from this derivative can be compared with that from conversion of a known amount of Aroclor 1254 to decachlorobiphenyl. This type of method is desirable for a monitoring program designed for rapid, inexpensive, and sensitive measurement of the total quantity of PCB without regard to composition. However, the development and usage of such a method would not preclude the need for the assay for individual PCBs.

Extracted PCB residues can be exhaustively chlorinated with chromous chloride or antimony pentachloride to decachlorobiphenyl and the electron capture signal of this compound can be compared to the EC signal of a known amount of a reference PCB mixture treated similarly (62). Aroclor 1254 has been chlorinated with antimony pentachloride and the resulting decachlorobiphenyl has been determined by GC (63).

Screening methods for PCDD residues based on their chlorination to octachlorodibenzo-p-dioxin, VI, have



VI

been developed (64, 65). The PCDD can be detected in the presence of PCB, PCN and PCDF. Chlorination with chlorine took place in the

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presence of iron filings and iodine. Ferric chloride - iodine (66) and antimony pentachloride (67) have been used as catalysts but were reported to give unsatisfactory results on the microgram scale (64). The recommended method consists of chlorination, liquid chromatography on alumina followed by electron capture GLC.

Another method of possibly quantitating the PCB as one entity involves carbon skeleton chromatography (68). The PCB residue is converted essentially into a mixture of cyclohexybenzene and biphenyl at a catalyst temperature of 300°, and into cyclohexylbenzene, and bicyclohexyl at 260°. The method needs further investigation and optimization. The technique may also be useful for confirmation purposes.

The formation of decachlorobiphenyl and its change into a measurable derivative by nucleophilic substitution reactions at the 4,4' - positions is another reaction that could be of value in developing an inexpensive monitoring method.

Confirmatory techniques are vital to assay methods for the environmental organic pollutants. The big problem is to identify component X in an environmental test sample. For the polychloro compounds assay is not enough; one must also be able to identify the pollutant unequivocally. In the majority of investigations one or more of four types of parameters have been used to identify trace amounts of organochlorine compounds: (1) GLC retention times using two or more stationary phases, (2) TLC R_f values using one or two systems, (3) preparation of derivatives and matching of the GLC retention times (and/or TLC R values) of the products with those of

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the known compounds, and (4) partition p-values. None of these procedures or their combinations are completely satisfactory to establish the identity of a component in an environmental sample. Since chemical identity at the submicro level is difficult, we will address ourselves to this problem.

The use of a double GC column system minimizes the risk of false identification, but GC alone cannot give an unequivocal identification. The use of GC with chemical treatment increases the certainty of the identification.

The uncertainties of identification are also confounded by the possibility that other halogens may be present in the PCB. Some of these compounds have been mentioned previously. Examples are trifluoropentachlorobiphenyls and trifluorotrichlorobiphenyls used in hydraulic fluids, and diaminopolyhalobiphenyls and dihydroxypolyhalobiphenyls used in the preparation of flame resistant polymers and reinforced plastics.

GLC has been the prime tool used in the analysis of organochlorine compounds, but it cannot give unequivocal characterization either with the help of retention indices, by the matching of retention time and peak height distribution with those of commercial products, by the use of halogen-specific microcoulometry to determine the presence of halogens in the compounds causing individual peaks, or by determining the resistance to attack by hot alcoholic KOH.

GLC-IR has also been used in identification studies (69). Identity was assumed if the synthetic PCB, when added to the Aroclor and chromatographed, enriched the appropriate peak and the IR spectrum

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of the synthetic isomer matched that of the isolated Aroclor isomer. Summary of the results are given in Tables II-6 and II-7.

With the help of carbon-skeleton chromatography PCB and biphenyl yield identical chromatograms that are different from those of DDT or other polychloro compounds (68).

Confirmation of identity can be achieved by combined GC-MS (70-72) which, in addition, yields the number of chlorine atoms per molecule (71). However, rearrangement of chlorine atoms on phenyl groups occurring in the electron-impact-induced fragmentation (7) limits the use of MS for structural studies. GC-MS does offer an excellent means of distinguishing PCN from pesticides and PCB (41). Identification of PCN has been made with the GC-MS system.

Mass spectrometric analysis has been used,even in the early work,to confirm the presence of PCB suggested by GLC data (21, 72). Although commercial PCB mixtures are complex, the mass spectra are relatively simple, since all isomers of a particular molecular composition give identical molecular ions (60), Figure II-8. The mass spectrum also reveals the typical isotope distribution pattern which is highly characteristic of the number of chlorine atoms present in the PCB isomers. The presence of these patterns facilitates identification of small quantities of PCB which may be present in a contaminated environmental mixture. The mass spectra of each set of isomeric compounds are similar and the fragmentation pattern of all the compounds from the dichlorobiphenyl isomers to decachlorobiphenyl feature successive expulsion of chlorine atoms and molecules, Fig. II-9,

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Table II-6. Summary of Aroclor GLC retention times and identities.

Retention Time[a]	Synthetic Chlorobiphenyl	Aroclor 1221	1232	1242	1248	1254
10	Biphenyl	X[b] C[c]	X	X	X	
13	2	X C	X	X	X	
16.9	3	X D[d]				
17	4	X C	X			
17.7				X		
18.6	2,2'	X C	X	X C	X	
21.3		X	X	X		
21.6		X	X	X		
23.6	2,3'	X C	X	X	X	
24	2,4'	X C	X	X C	X	
26	2,6,2'		X	X D	X	
29	2,5,2'		X	X C	X	
29.2	2,4,2'	X	X	X C	X	
29.5	4,4'	X C	X	C		
34	2,3,2'		X	X C[e]	X	
38	2,4,3'		X	X C	X	
38.5	2,4,4'		X	X C	X	
38.7	2,5,4'		X	X C	X	
41.5				X	X	
42.5	3,4,2'			X C	X	
43				X	X	
44				X	X	
44.5					X	
48	2,5,2',5'			X C	X	X C
49.5	2,4,2',5'			X C	X	X C
50.5	2,4,2',4'			X D	X	
51.5				X	X	
55	2,3,2',5'			X	X	X C
57				X	X	
59	2,3,6,2',6'			X	X	X D

(Continued)

Table II-6 (Continued)

Retention Time[a]	Synthetic Chlorobiphenyl[b]	Aroclor 1221	1232	1242	1248	1254
60				X	X	
64				X	X	
69				X	X	
69.5					X	X
70	2,6,3',4'			X C[c]	X	
70.5	2,3,6,2',6'					X C
71	2,4,3',4'			X C[c]	X	
72				X	X	
76	2,3,6,2',4'					X C
82					X	
83	2,3,6,2',3'				X	X C
84					X	
85	2,4,5,2',5'				X	X C
87	2,4,5,2',4'				X	X C
96	D[e]					X
99	2,4,6,2',3'				X	X C
101					X	X
104					X	X
107	2,3,6,3',4'				X	X
115						X
117					X	X
119						X
125	2,4,5,2',3',6'					X C
126	2,4,6,3',4'				X	X C
135						X
147						X
149	2,4,5,2',4',5'					X C
149						X
152						X
165						X
178						X

[a] Relative to p,p'-DDE at 190°C on 100' × 0.02" SCOT SE-30 column.

[b] X indicates a GLC peak in this Aroclor at this retention time.

[c] C means that the synthetic compound in the second column was confirmed by GLC and IR in this Aroclor. Because of the labor involved, most compounds were only confirmed in one Aroclor. For example, biphenyl is probably present in 1232-1248 as well as 1221.

[d] Only GLC data available.

[e] Something else also present.

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Table II-7. PCB Isomers Found To Be Absent from Aroclors 1221-1254.

Chlorobiphenyl	Retention Time*
2,3,4'	44
3,4,4'	59.5
2,5,3'	36
3,5,3'	46
2,6,3'	32
2,3,2',4'	57
2,3,3',5'	66
2,3,2',6'	47
2,3,5,2',3'	63
2,3,5,2',4'	65
2,3,5,2',5'	83
2,3,5,2',6'	68
2,3,5,3',4'	121
2,4,5,2',5'	70.5
2,4,5,3',5'	104
2,4,6,2',4'	65
2,4,6,2',4',6'	76
2,3,5,2',3',5'	138
2,3,5,2',4',5'	142
2,3,5,2',3',6'	116

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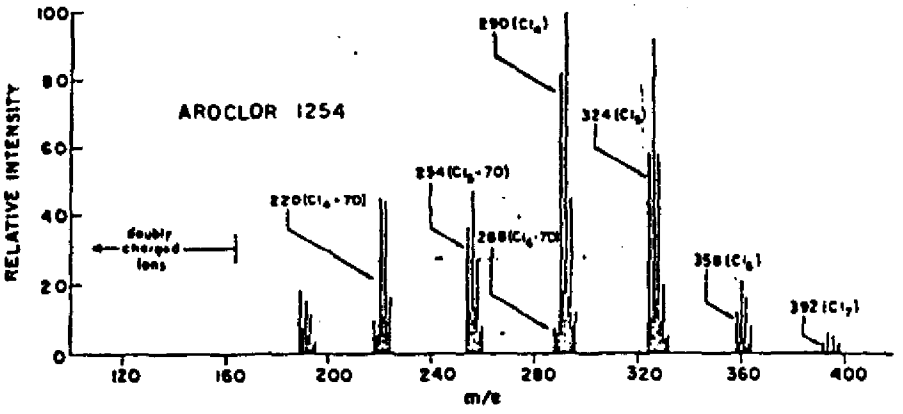

Figure II-8. Mass Spectrum of Aroclor 1254.

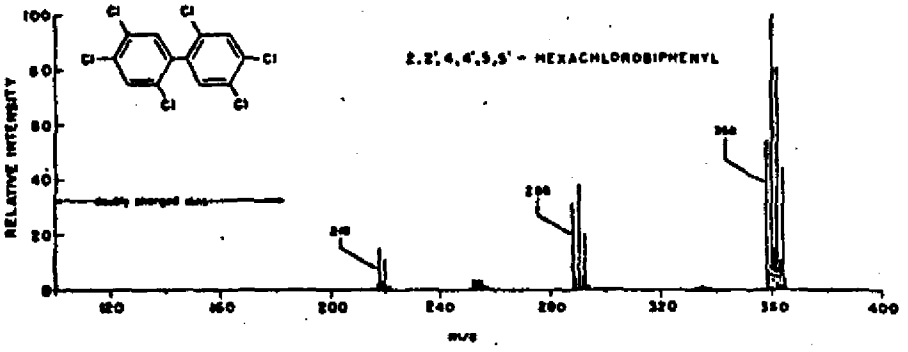

Figure II-9. Mass Spectrum of 2,2',4,4',5,5' - Hexachlorobiphenyl.

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with elimination of HCl from the less chlorinated homologues also evident (60).

The molecular-ion peaks of the major biphenyl components are easily distinguishable from those of the most common chlorinated pesticides (73). For mixtures, it is possible to obtain separate spectra by using a controlled temperature probe and by operating at the temperature at which the components fractionally sublime; for the PCB and DDT these are 24° and 67°, respectively.

Nuclear-magnetic-resonance spectroscopy has also been used to resolve the structures of some of the PCB isomers (74). Unequivocal characterization of the components of technical PCB mixtures has also been claimed based on the criteria of the availability of the pure standard, GLC retention times on three different GLC columns, infrared spectra and NMR spectra (75).

Some of the reactions of the fully chlorinated PCB, etc. could be developed into confirmatory tests (76). Thus, decachlorobiphenyl reacts at the 4,4'-positions in nucleophilic substitution reactions. The halogens in these positions are activated so that they can be substituted by more eletropositive groupings.

Ultraviolet absorption spectra are also useful in confirming the basic ring structure. The PCN can be differentiated from the other polychloro compounds by the long wavelength band at 305 nm. The PCDF have a very characteristic UV spectrum. The spectra of the PCDD are given in Table II-8 (24). In addition, the PCDDs give a blue color reaction in concentra H_2SO_4 when treated with an oxidizing agent such as potassium nitrate (66,77).

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Table II-8. Ultraviolet Spectral Data for Chlorinated Dibenzo-p-dioxins

Dibenzo-*p*-dioxin	$CHCl_3$				
	λ	ε	λ	ε'	ε/ε'
Unsubstituted	248	1020	293	3680	0.278
1-Chloro-	248	1320	294	3190	0.414
2-Chloro-	248	1140	299	3700	0.308
2,7-Dichloro-	247	1340	302	4590	0.292
2,8-Dichloro-	247	1180	299	4690	0.252
2,3-Dichloro-	247	1830	304	3190	0.573
1,2,4-Trichloro-	253	5290	294	2250	2.36
1,2,3,4-Tetrachloro-	257	6290	317	2290	2.75
2,3,7,8-Tetrachloro-	248	2970	310	5590	0.532
1,3,6,8-Tetrachloro-	250	5540	305	3440	1.61
1,2,3,4,7-Pentachloro-	259	5920	306	2690	2.20
1,2,3,4,7,8-Hexachloro-	259	5370	316	3660	1.47
1,2,4,6,7,9-Hexachloro-	259	4450	310	1480	3.01
Octachloro-	261	13150	318	2400	5.48

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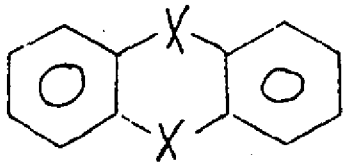
formation of a highly colored cation radical is characteristic of compounds of structure VII, where X can be O, S, Se or Te.



VII

The PCDDs also show widely varying phosphorescent spectra which can be used in characterization studies, (See Table II-9). In addition, all of the isomers are distinguished easily from one another by their infrared spectra and the PCDDs can be distinguished from the PCDF and PCDE by their characteristic mass spectral fragmentation patterns.

Confirmation of the structure of the PCB isomers could also be accomplished with the help of pulsed source-time resolved phosphorimetry (61).

C. Air

The vapor pressures, boiling points and distillation ranges of PCB technical mixtures give an indication which of these compounds will be found in the vapor phase and or in the particulate phase in the air (78). Thus, the distillation ranges of the Aroclors vary from 275 - 320° for Aroclor 1221 to 435 - 450° for Aroclor 1268. Anthracene and phenanthrene boil at 341 and 338°, respectively, and are probably present in the atmosphere in the vapor phase since

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Table II-9. Phosphorescence Spectral Data for Chlorodibenzo-p-dioxins

Dibenzo-*p*-dioxin	Excitation, λ (nm)	Emission bands, λ (nm)
Unsubstituted	294	386, 395,[a] 410, 418, 426,[a] 438
1-Chloro-	296	396, 402,[a] 422, 430[b]
2-Chloro-	295	400,[a] 420
2,7-Dichloro-	300	404,[a] 412, 426, 433, 458, 465
2,8-Dichloro-	304	400,[a] 404,[b] 412, 420, 428, 432, 440, 450, 458
2,3-Dichloro-	312	408, 418, 435[a]
1,2,4-Trichloro-	304	412,[a] 418,[b] 427, 439[a]
1,2,3,4-Tetrachloro-	304	485[a] (very broad)
2,3,7,8-Tetrachloro-	305	411,[a] 418, 422, 436, 440, 448, 468
1,3,6,8-Tetrachloro-	300	410,[a] 418, 433, 438, 465
Octachloro-	310	433,[a] 458, 490

[a] Strongest peak. [b] Peak not resolved.

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they are not usually collected on glass fiber paper with a high volume sampler. Anyway, as far as this type of collection is concerned, they are atmospheric vapors. This would mean that Aroclor 1221 also could not be collected in this fashion. Fluoranthene, pyrene and chrysene have boiling points of 384°, 394° and 441°, respectively, and are probably mainly collected as particulate with a large portion not collected by the filter. This means that Aroclor 1268 could be only partially collected as particulate.

The importance of PCB in the atmosphere derives from the spread of the PCB by air transport. The following sources are of importance - (a) Manufacturing in the Sauget, Illinois ~~St. Louis and Anniston, Alabama~~ no longer plants of the Monsanto Co., (b) Evaporation from incineration of refuse that contains PCB, (c) Use and wear of PCB containing materials, (d) Leakage from closed systems, (e) Open air burning, (f) Fine spray mist from the concentrated monomolecular layer of the oceans and other bodies of water.

In a study of air over the North Atlantic ocean and in Bermuda PCB could only be found in the vapor phase (79). None were found in the particulates, although PCBs have been reported in selected urban airborne particulate samples. A large amount of PCBs must get into the air since it has been shown that 81% of incinerator workers have PCB in their blood plasma (81).

Collection of PCBs has been accomplished by passage of air at 20-30 CFM through ceramic chips coated with 0.1% OV-17 (79). PCB were not

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detected in a sample of marine air taken off the California coast (82). However, PCB fallout has been reported in southern Sweden. PCBs also have been detected in black snow in southern Sweden.

Certainly, a variety of good analytical techniques are now available for the PCBs which could easily be applied to air analysis, but a good sampling method for atmospheric PCBs needs to be developed

D. Water

The solubilities and the partition coefficients of the PCB are of prime importance in understanding the distribution of the PCB in aqueous systems. These physical constants have been discussed (84). Because of their low solubility and high adsorbability most of the PCB could be expected to be present in aqueous sludges or sediments. Similarly, tetrachloro DD, like DDT and higher PCB is soluble to the extent of 0.2 ppb and is strongly adsorbed on clay and organic matter. The solubilization of PCB in water by non-ionic surfactants as well as the determination of concentration of the solubilized PCB by UV spectrophotometry, fluorescence and GLC has been described (85).

Sampling of water solutions of the PCB has been accomplished by extraction with organic solvents (86), adsorption on activated carbon (87), collection by reversed phase liquid-liquid partition (88), collection on a porous polyurethane foam (89), and passage through a 3g. filter containing a mixture of n-undecane and Carbowax 4000 monostearate on Chromsorb W (88). Extraction is time-consuming and needs to be done in the laboratory. However, the process can be

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considerably speeded up and made more efficient by means of ultrasonic extraction. Recovery from charcoal is variable and inefficient and the recovered material may be significantly different from the initial PCB. The reversed liquid-liquid partition filter gives excellent recoveries but is limited by low flow rates and requires elaborate preparation.

A recent method for collection and elution of PCB (89a) from seawater utilizes Amberlite XAD-2 Resin (XAD-2) (89b), a synthetic polymer of styrene and divinylbenzene which is further crosslinked and formulated into 20-50 mesh white beads. The claimed advantages of this material as compared to polyurethane and reversed phase liquid-liquid chromatography are that: (a) it is not compressible even at a depth of 1000 m, (b) there is no organic coating on the XAD-2 so that after elution of the column, it is ready to be reused, (c) chlorinated hydrocarbons are readily adsorbed from seawater, and (d) they are readily eluted quantitatively by 4 bed volumes of acetonitrile or ethanol.

Material collected on a solid material can be eluted with petroleum ether, cyclohexane or with acetone and hexane or ether and hexane. If necessary ultrasonics can be used to speed up the extraction. Another possibility is direct sublimation into the GC. Ultrasonic extraction and sublimation have been found to be useful in our laboratories in the analysis of atmospheric PAH.

Although the extraction of PCB from sewage solids using a mixture of n-hexane and isopropanol is probably less efficient than extraction from water, many sludge samples were found to

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give gas-liquid chromatograms similar to those of PCB mixtures (90). Aliquots of concentrated extracts of California coastal waters contaminated by PCB from urban sewage outfalls have been analyzed by GLC using a ^{63}Ni electron capture detector and a 3% QF-1 column on 80 - 100 mesh, acid-washed, DMCS-treated Chromosorb (91).

The occurrence and distribution of the PCB in the River Rhine and the coastal areas of The Netherlands have been studied with the help of GC-MS (21). Computer-controlled GC-MS has been used to identify tetrachlorobiphenyls in a Los Angeles sewer extract (92). The sensitivity of the method for aqueous PCB based on reversed phase liquid-liquid partition between water and Chromosorb W (coated with n-undecane and Carbowax 4000) is in the ppt range (88).

Highly sensitive and reliable methods are needed for analysis of water samples especially those obtained from the ocean since it has been reported that aqueous concentrations in the North Atlantic are 35 ppt at the surface, 10 ppt at 200 meters and traces at 3000 meters (79). The lack of systematic analytical procedures for the characterization and determination of PCB in natural waters has been pointed out in a recent review (93).

E. Soil

Very little work has been done in the study of the contamination of soil with PCB. It has been estimated that the half life of PCB soil is of the order of five years while tetrachlorodibenzo-p-dioxin appears to have a long life in soil. The persistence of pesticides

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in soil has aroused considerable interest in recent years, as evidenced by soil monitoring activities at local and national levels (94 - 98). The extraction of residues from soil is as important as their determination since residues not extracted are not measured. The usual extraction methods make no provision for rupturing cells and liberating bound residues. Ultrasonic extraction has been used to obtain insecticides from soil (99) and polynuclear aromatic hydrocarbons from air particulate samples (100) efficiently and quickly. The PCB could be extracted in the same way from the various types of soil samples and further cleanup, characterization and assay would be by some of the procedures previously described.

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F. Food and Biological Tissues

1. Introduction

The sampling and analysis of polychlorobiphenyls in biological tissues is essential for the establishment of the extent of their deposition and distribution in the biosphere. The food chain probably represents the major source of man's exposure to PCB's. This supposition can only be confirmed when the levels of PCB's in the environmental media, in man's food and in man himself can be accurately determined and correlated. The deposition, retention and metabolism of PCB's in the human body must be determined before the potential hazard to human health can be assessed. Measurement of PCB residues in wildlife is likewise necessary to ascertain what biota serve as "sinks" for PCB's and to what extent PCB's are a threat to the ecosystem.

While different sampling methods may be required for different biological specimens, the isolation, cleanup and analysis methodologies for PCB's in foods and in plant, animal and human tissues and fluids will be essentially similar. For this reason, these laboratory procedures will be discussed in general and pertinent information regarding specific sampling and analysis techniques will be discussed separately.

2. Isolation, Cleanup and Analysis

Polychlorobiphenyls are chemically similar to organochlorine insecticides. The methods of extraction, cleanup

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and determination developed over many years for organochlorine pesticides are, for the most part, also satisfactory for PCB's. PCB's readily pass through the analytical schemes designed for the recovery of pesticides from plant and animal tissues and when present in sufficient quantities interfere with the determination of many of the chlorinated pesticides. In fact, the existence of PCB's in the environment was first discovered in this way(2) and PCB "contamination" continues to plague the pesticide residue chemist. Several means of eliminating this mutual interference have been developed in recent years.

(a) Pesticides Residue Analysis

The most generally accepted methods for determination of organochlorine pesticides in biological tissues are those published by the U.S. Department of Health, Education and Welfare, Food and Drug Administration, in their Pesticide Analytical Manual(101). There are essentially two procedures:

(i) For fatty tissue (both animal and plant), the pesticides are extracted (along with lipids) from the ground or chopped specimen with an organic solvent such as hexane. The pesticides are then separated from the lipids by liquid-liquid partitioning into acetonitrile. Column chromatography on activated Florisil (a magnesia-silica gel adsorbant manufactured by the Floridin Company, Pittsburgh, Pennsylvania) is then utilized to remove remaining lipids and to fractionate the pesticides into groups to facilitate their identification. Finally fractions from the Florisil column are analyzed by gas chromatography coupled with an appropriate detector.

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Organochlorine pesticides can be identified and quantitatively measured by either of two chlorine-specific detectors, the electrolytic conductivity detector (102) or the microcoulometric titrator (103). However, due to the relatively low sensitivity of these detectors (10-50 ng minimum detection limits), the non-specific electron capture detector (5 to 100 pg minimum detectability, ref. 104 is more often used.

(ii) Non-fatty tissues (less than 10% fat) are usually extracted directly with acetonitrile or some other solvents. Otherwise, the methodology is the same as that for fatty tissues.

(b) Separation of PCB's from Pesticides

In these procedures, polychlorobiphenyls are extracted from plant and animal tissues along with any pesticides present. Some losses may result on acetonitrile partitioning, however. Risebrough (105) cautioned that as much as 30% of the rather nonpolar PCB's may remain behind in the hexane layer. Reports of nearly quantitative recoveries of Aroclors from fatty foods (29) suggest that efficient partitioning is possible. It should be noted that the FDA procedure (101) calls for partitioning four times. Recoveries of nonpolar pesticides such as aldrin are only about 70% after the first partitioning. Chromatography on Florisil will not allow separation of PCB's from many organochlorine insecticides. The PCB's are eluted in the first fraction (6% diethyl ether in petroleum ether or 20% methylene

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chloride in hexane, depending on the method used) along with most of the organochlorine pesticide group. Initial elution with n-hexane has been used to effect a partial separation (21,28) but for the complete separation required for analysis further steps are necessary.

The problem of separating PCB's from chlorinated pesticides has been approached successfully from several directions. The separation may be accomplished either by physical or chemical means.

(i) Physical separations have been primarily accomplished by liquid-solid absorption chromatography, often in conjunction with Florisil cleanup chromatography. Holden and Marsden reported success with alumina and silica gel (27). Synder and Reinert found silica gel to be effective in separating Aroclors 1254 and 1260 from DDT and its metabolites (106). Gel permeation chromatography has been recently reported to be efficient and reproducible for both cleanup and separation of PCB's from organochlorine pesticides (107). A still more recent paper describes the use of activated charcoal (63). Extracts are adsorbed in a column of cocoanut charcoal. An ether-acetone mixture is used to remove the DDT group of pesticides (with 91-94% efficiency) and benzene serves to elute PCB's (90% efficiency). Oils or fatty extracts can be removed by Florisil cleanup after the charcoal separation.

A technique developed by Armour and Burke of the FDA (29) has now been incorporated into the Pesticide

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Analytical Manual (108). This technique employs column chromatography on silicic acid-Celite after the Florisil cleanup.

Thin-layer chromatography has also been used to separate PCB's from pesticides. Probably the most widely used method is that of Mulhern et al. (35). After Florisil cleanup, the 6% ether-pct-ether fraction is thin-layer chromatographed on alumina G impregnated with silver nitrate. The PCB's accumulate in one spot, visible after exposure to ultraviolet light, and are estimated semi-quantitatively by visual comparison to a standard of Aroclor 1260. Another method is based on two-dimensional thin-layer chromatography (38).

Reversed-phase paper chromatography has also been used successfully to separate PCB's from chlorinated pesticides and their metabolites (109). The former exhibit much lower R_f values.

(ii) The other means by which interferences by some organochlorine pesticides can be eliminated is by chemical alteration. The PCB's resist alteration due to their high chemical stability. The most common methods used are nitration (28,110) and dehydro-chlorination of the pesticides (111). Both of these methods have draw-backs in that they do not eliminate all chlorinated pesticides; the products produced may have long GC retention times and thereby cause analytical problems; and some of the PCB isomers may also be altered. Treatment with fuming nitric

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acid is known to nitrate some of the lower chlorinated biphenyls and will not affect some pesticides, such as toxaphene, lindane, γ-BHC or strobane (112) Dehydrochlorination with alcoholic potassium hydroxide will eliminate DDT and DDD, but not the important interferent DDE (in fact, it may produce it). Fuming sulfuric acid can also be used to eliminate interference by aldrin, DDT, DDD and DDE, but not lindane or heptochlor epoxide (88).

A recently reported method takes advantage of the high thermal stabilities of PCB's to eliminate them as interferences in the determination of organochlorine pesticides (113). In the Coulson electrolytic conductivity detector chlorine-containing organic compounds are pyrolyzed in a hydrogen atmosphere as they exit from the gas chromatograph. The hydrogen chloride produced is passed through de-ionized water and measurement of electrical conductivity is used to determine the initial amount of compound present. Under the normal operating conditions (850°C), both PCB's and chlorinated pesticides are pyrolyzed. However, at 600°C, the PCB's are not burned and will, therefore, produce no response. In this manner, PCB's may be determined by differences.

c. Quantification

Once PCB's have been isolated from biological media and interfering organochlorine pesticides, the problem then arises as to how to quantify them. There are 210 possible compounds of mono- to decachlorinated biphenyl (72).

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Commercial preparations, such as the Aroclors, are complex mixtures of many chlorinated biphenyls. A gas chromatogram of a given Aroclor will reveal many peaks and any given peak may represent a number of different isomers and/or chlorine homologs of chlorinated biphenyls. Once released into the environment, the composition of a commercial preparation will change since the different PCB compounds contained therein have different volatilities, solubilities and stabilities to chemical and metabolic breakdown. It is highly unlikely, for example, that Aroclor 1254 will be found in any environmental sample. A distribution of PCB's tending to match an Aroclor 1254 standard may be detected, but that would not mean that the sample was exposed to that particular Aroclor. In fact, even the composition of Aroclor 1254 (or any other Aroclor) will vary slightly from batch to batch. Yet, for lack of better methodology or lack of understanding, nearly all residue analysts in the United States try to identify and quantify PCB residues as particular Aroclors.

Estimation is usually accomplished by:

(i) "Fingerprint matching" with a known PCB standard and summation of all components detected (114);

(ii) Using the average of two peaks (28);

(iii) Comparison to p,p'-DDE using electron capture detection (30); or

(iv) Comparison to the peak in Phenoclor DP6 which has a retention time relative to dieldrin of 1.45 (21).

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Electron capture detection (ECD) is most often used in each case. Another method which is perhaps better is that of Rote and Murphy (20). These investigators prepared electron capture response curves of total peak area per nanogram for six Aroclors versus the average number of chlorine atoms per molecule for each Aroclor. Unknowns were then compared to this response curve for identification and quantification. Of course, such response curves would have to be prepared frequently to assure accuracy.

In all of these methods, as well as in the thin-layer chromatographic methods previously mentioned, the PCB's are determined as an Aroclor (or its European or Japanese counterpart), which has no real meaning.

Isomeric groups of polychlorobiphenyls can be detected by mass spectroscopy. It is possible, therefore, to determine the amounts of tetrachloro-, pentachloro-, hexachlorobiphenyls, etc. in a PCB mixture (92,115). By combined gas chromatography-mass spectroscopy (GC-MS), the molecular weight and chlorine number associated with each peak can be ascertained. Elucidation of the structures of the many individual isomers is a very difficult task, particularly since chromatographic separation prior to analysis is not possible.

Perhaps the most valuable application of mass spectroscopy to PCB and pesticide residue analysis is as a confirmatory tool. Although GC-MS is one or more orders of magnitude less sensitive than GC-ECD for PCB's, it has sensitivity

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as good or better than other chlorine-sensitive detectors and it is far more specific. Mass spectroscopy is often the only way by which the identity of a trace pollutant can be established. Mass spectrometers are not, however, simple to operate. Computer operation and data interpretation is usually required, with very expensive instrumentation the result.

The problem of the multi-component nature of PCB's can be circumvented by chemical conversion to a single compound and at the same time a large increase in sensitivity can be achieved. There are two methods: dechlorination to biphenyl (63,116,68) and perchlorination to decachlorobiphenyl (63). By these methods all isomers and chlorine homologs are converted on one chemical entity which allows determination of the total PCB content of the sample. Problems with identification, interference and detection limits are reduced since one peak instead of many is obtained from the gas chromatograph. Dechlorination (usually with hydrogen over platinum or palladium) is less advantageous in that the product is a hydrocarbon and can be measured only at a relatively low level of sensitivity. Perchlorination with antimony pentachloride yields fully chlorinated biphenyl for which chlorine-specific and electron capture detectors should be most sensitive. At the microgram level yields are reported to be 85 ± 5% (63). On gas chromatography using SE-30, the decachlorobiphenyl peak is well removed from those of common chlorinated pesticides (44). The perchlorination procedure, therefore, offers

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much promise for the solution of the complicated problems of analysis and quantification of PCB's. Confirmatory analysis, usually very difficult at the residue level, is also greatly simplified.

3. Foods

Extraction and cleanup methodologies suitable for analysis of PCB residues in food products are provided in detail in the FDA's Pesticide Analytical Manual (101); the USDA's Chemistry Laboratory Guidebook (117), the "Guide to the Analysis of Pesticide Residues" published by the U. S. Public Health Service (118), the Canadian Food and Drug Directorate's "Analytical Methods for Pesticide Residues in Foods" (119), and the Official Methods of Analysis of the Associates of Official Analytical Chemists (120).

Instructions for the collection of food and feed samples for pesticide residue analysis are given in the FDA Inspectors Programs Manual. Total composite samples of approximately 20 pounds are collected from retail units, warehouses and transport vehicles. Additional specifications are given for sample sizes for selective samples such as raw agricultural products, milk, eggs, meat, etc.

The Manual also covers sample preparation, as does the Pesticide Analytical Manual (ref.101, Section 141). Inedible and decomposed parts, soil, waxes, etc., are removed from raw agricultural products and discarded. In the case of processed foods, packing liquors are analyzed only if

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normally consumed and dehydrated or concentrated foods are not reconstituted prior to analysis. Meats and other fatty foods are ground or blended, usually with anhydrous sodium sulfate for drying, and extracted with petroleum ether. The extract is dried to recover the fat. The fat is then redissolved in a minimum quantity of petroluem ether and the pesticides (or PCB's) are partitioned out into acetonitrile. Cleanup and separation procedures described previously are utilized. Sweep-codistillation of pesticidal compounds from edible fats and oils is sometimes employed (121). Non-fatty foods (fruit, green vegetables, berries, corn meal, potatoes, wheat, etc.) are analyzed in much the same manner. The primary difference is that extraction and partitioning are done in one step. The commodity is usually blended with acetonitrile, filtered, sodium chloride solution added, and then extraction with petroluem ether is carried out. Milk requires some special treatment. Whole milk is mixed with an equal volume of ethanol or methanol and sodium or potassium oxalate is added. After further dilution with aqueous sodium chloride, it is extracted with a 1:1 mixture of petroleum ether and diethyl ether. Partitioning into acetonitrile and Florisil cleanup follows this treatment.

The latest addition to Volume I of the FDA Pesticide Analytical Manual describes a method for exhaustive extraction of organochlorine residues in foods and feeds (Section 253, September 1, 1972). Soxhlet extraction is employed in place of cold extraction for solid foods. A 1:1 mixture of chloroform and methanol is substituted for petroleum ether.

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The method was first reported by Porter et al. (50) for fish, meat and poultry.

Cold extraction with a 1:1 mixture of hexane and isopropanol, followed by benzene, was used by Skrentny et al. (122) to recover PCB's from homogenized corn silage. Florisil chromatography was employed for cleanup, with elution by hexane used to partially separate the PCB's from chlorinated pesticides.

Bellman and Barry (123) applied combined gas chromatography-mass spectroscopy to the determination of PCB's in several food products. The standard FDA isolation and cleanup methodologies were utilized. However, these investigators were unable to detect PCB's in any samples.

In the examination of food commodities as sources of polychlorobiphenyl injestion by humans, it would seem to be advisable to prepare the foods sampled in the manner in which they are normally prepared for consumption. Although PCB's are quite stable thermally and have only slight water solubilities, there is undoubtedly some loss on cooking. When only trace quantities are present, these losses could be very significant. This problem does not appear to have been addressed in the literature.

4. Animal Tissues

Most sampling of animal life for polychlorobiphenyl determination has been on marine fauna and predatory birds (especially sea birds). There is no standard for collection of tissue specimens ... little ... to compare

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the same types of tissues in different species of animals.

Adipose tissue (fat) appears to be a repository for PCB's in animals, although high levels have also been found in liver of the white sharks (124). Some animals possess two types of adipose (brown and white) in which the rates of metabolism differ greatly. For an accurate assessment of PCB residues in animals, careful consideration must be given to the selection of tissue(s).

Methods of preservation of specimens between collection and analysis have varied from study to study. Some analyses have been performed on animals in rather advanced states of decay (57). Although PCB's are generally quite resistant to degradation, chemical and bacteria breakdown in unpreserved samples could result in losses. Other decay products may also interfere with PCB determinations. Tissue or whole specimens should, therefore, be frozen, preferably with Dry Ice, until analyzed. Under no circumstances should chemical preservatives such as formaldehyde be used. Care should also be given to selection of storage vessels. Contamination by PCB's or other interfering organics could result from storage in plastic containers (although polyethylene bags may be acceptable).

Preparation of samples for analysis also varies greatly. Samples may be extracted wet (with quantification of data based on wet weight) or lyophilized before analysis. It is desirable to determine residue levels in terms of dry weight;

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however, drying by lyophilization may result of losses from volatilization. In the analysis of fatty tissues, the fat can be extracted along with the PCB's, separated and weighed for quantification of the PCB's in terms of dry weight of adipose tissue.

Analytically, the same methodologies which apply to the determination of organochlorine residues in fatty foods should serve equally well for all animal tissues. In addition, the FDA Pesticide Analytical Manual offers a general method for determination of chlorinated organic residues in human or animal adipose tissue (Volume III, Section HE211). This method is discussed under Section III, 6 of this paper.

Duke et al. (125) analyzed fish, crabs, and oysters for PCB's using essentially the FDA procedure for foods except that extractions (with petroleum ether) were carried out in Soxhlet apparatus. These investigators reported the PCB's found in the first fraction from the Florisil cleanup as Aroclor 1254.

Koemen et al. (21) used nearly the same method in isolating and determining PCB's in fish, mussels and birds. In this case dimethyl-formamide was substituted for acetonitrile in the partitioning step. DeVos and Koeman also employed the same technique for chickens (126).

Armour and Burke (29), Synder and Reinert (106) and Zitko (127) used silicic acid chromatography, following conventional cleanup methodologies, to separate PCB's from chlorinated pesticides in the analysis of various species of

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fish. Zitko et al. (124) utilized the same methodology in the analysis of mussels, liver, fat and other tissues from fish and sea birds and their eggs.

Gel permeation chromatography has been employed and Stalling et al. (107,128) for preparation of fish samples for PCB analysis (See Section III, 2).

Risebrough (56) removed DDT compounds as interferences in the determination of PCB's in birds and fish by nitration and saponification, then quantified the PCB's by comparison to a p,p'-DDE standard using electron capture detection and microcoulometry.

Grant et al. (54) analyzed blood, liver, kidney, testes, heart, brain, spleen and fat samples from rats dosed with Aroclor 1254. Tissues were blended with hexane and anhydrous sodium sulfate, and the extracts were treated with fuming sulfuric acid before analysis by GC-ECD. PCB concentrations were calculated on the basis of wet tissue weights.

Liver samples taken from sea otters were digested in a perchloric-acetic acid mixture and the fat extracted with hexane in work reported by Rote and Murphy (20). FDA cleanup procedures and silicic acid-Celite separation were used.

Destructive chemical treatments such as those employed in the previous three studies are risky in that some unwanted alteration of PCB's may be effected.

Widely different results may be obtained with different methods of quantification. For example, Risebrough and de Lappe (103) quantified PCB's in bird eggs by the common term

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using two different methods. When the areas of PCB peaks emerging after p,p'-DDE on the gas chromatogram (ECD) were compared with an Aroclor 1254 standard, concentrations of 308 and 214 ppm were calculated for the egg lipids. Comparison of the areas to the total area of the same peaks in an Aroclor 1260 standard, the values obtained were less than one-half of those calculated by the first method. Various quantitation techniques can lead, therefore, to widely differing results between laboratories.

PCB concentrations in Atlantic zooplankton were also reported by the above investigators (129). Levels ranging from 2 to 260 ppm were measured in lipids extracted with 2:1 hexane:acetone in a Soxhlet apparatus.

5. Plant Tissues

Most reports of PCB determinations in plant tissues have been on raw agricultural food products. Very little examination of non-agricultural flora has been undertaken.

Suitable analytical methodologies would be those designed for non-fatty foods discussed in Section III, 2 and III, 3 of this paper. Collection procedures would depend on the nature of the study. If environmental transport via food chains is of principal concern, plant life which serve as primary food sources for animal wildlife would be sampled. Edible portions would be taken, preserved and prepared for analysis. Preservation of plant samples is generally less troublesome than that of animal specimens,

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since decay is less rapid in the former. However, samples should be kept cool or preferably frozen until ready for analysis.

Perhaps the most important plant life for PCB accumulation and distribution along the food chain is marine flora. The common marine phytoplankton Cylindrotheca closterium has been found to concentrate PCB's present in water by a thousand-fold or more. Fish feeding on this diatom receive far more PCB's than they would otherwise extract from water and pass them along to man and other fish-eating animals. Keil et al. (52) determined the uptake of Aroclor 1242 by C. closterium by lyophilizing the sample, extracting with acetone and analyzing by gas chromatography. Identification was achieved by comparison of the relative retention times of the five major peaks. As previously mentioned, lyophilization could have resulted in losses of some PCB's from the sample and should be avoided. Centrifugation or filtration followed by air drying would have been preferable. It should be mentioned here that there is some evidence (52) that PCB's may inhibit photosynthesis in marine phytoplankton, which represent an important contribution to the world oxygen reserve. Varying sampling techniques for ocean plankton can lead to poor reproducibility and other problems (130). Samples are usually collected in nets. Mesh sizes vary and often no attempt is made to exclude sea-surface debris. Paint, oil and tar particles may be collected in the process.

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6. Human Tissues and Fluids

Analytical methodologies suitable for PCB assay in human tissues are described in Section III, 2 and III, 4 of this paper. In addition, Volume III of the FDA Pesticide Analytical Manual (131) is concerned with methods for organochlorine residues in human media. The U. S. Environmental Protection Agency has also conducted a nationwide human monitoring program for pesticides and PCB's (132). Analytical methods for that program have also been published (133).

The most commonly used method for isolation and cleanup of PCB's for human tissue is a modification of one devised by Mills (134) for pesticides in adipose tissue. The procedure is detailed in the Pesticide Analytical Manual (131). Adipose is ground with anhydrous sodium sulfate and sand, extracted with petroleum ether, filtered and weighed. The lipid extract is redissolved in petroleum ether and the organochlorine compounds are extracted into acetonitrile by liquid-liquid partitioning. Further cleanup and fractionation is accomplished by conventional Florisil chromatography. Polychlorobiphenyls and nonpolar organochlorine pesticides are eluted from the Florisil column with a mixture of 6% diethyl ether in petroleum ether. The chlorinated pesticides are removed by chromatography on silicic acid. The same or similar methodologies are applicable to liver, kidney, bone marrow, adrenal, gonads, brain and blood.

When tissue quantity is limited or when levels of chlorin[illegible] is

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available (131). As little as 50 mg of tissue may be available from autopsy and biopsy samples. With the micro procedure 10 ppb of a given organochlorine compound can be detected on this size sample. The main difference between the micro and full-scale methods is a revisal of the extraction and partitioning schemes. In the micro method, acetonitrile is used for extraction, which in turn is diluted with water, and the pesticides and PCB's are then partitioned into hexane. Chromatography on a micro Florisil column calls for elution with hexane, followed by 1% methanol in hexane. For brain tissue, the concentrated hexane extract is treated with acetic anhydride and pyridine at 60-65°C, probably to release phospholipids.

Biros et al. (70) utilized the modified Mills procedure (131,134) to isolate PCB's from human adipose tissue. The presence of PCB's was determined by electron capture and microcoulometric gas chromatography and mass spectroscopy was used for identification and quantitation. These workers used a stainless steel capillary column coated with OV-1 in their GC-MS studies. It should be pointed out that organochlorine compounds can decompose on hot stainless steel surfaces so that caution should be exercised in using this method.

In a Japanese study (135) PCB's were determined in the skin of a still-born infant poisoned by Kanechlor 400 (a mixture of di-, tri-, tetra- and pentachlorobiphenyl with an average chlorine content of 40%). The tissue was chopped

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into small pieces and extracted separately with ethanol, ether and hexane. Partitioning into acetonitrile and Florisil cleanup were then carried out according to FDA procedures (131).

Collection of tissue samples from human beings is somewhat more complicated than in the case of wildlife. Sufficient quantities of tissues are rarely available from living subjects. Hair and body fluids are readily available but do represent ideal media for assessing PCB uptake and accumulation by humans. Autopsy materials, therefore, offer the best source for such studies.

The question then arises as to what tissues to sample and from what portion of the organ they should be taken. On this question, there seems to be considerable disagreement among biochemists, pathologists and others.

A recent protocol for the collection of autopsy tissue sets has been established by the U. S. Environmental Protection Agency for the Community Health and Environmental Surveillance System (136). This protocol calls for the 19 different tissues, including hair, fat, muscle, bone and vital organs, from autopsies. Stillborns, victims of homocides, suicides, accidental poisonings and embalmed bodies are excluded. Tissues are placed into Ziploc® plastic bags (polyethylene) and frozen as soon as possible after removal from the body. (Comments regarding sample preservation and preparation for analysis are presented in Section III, 4 of this paper). [illegible] for the autopsy.

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Since it is often not possible or desirable to collect and/or analyze an entire organ, consideration was given as to what portion of that organ should be sampled in order to provide a representative specimen. On this there is little agreement apparent among workers in the field (137). For pollutant accumulation and storage studies, however, agreement that subcutaneous fat from the peritoneum is most valuable.

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G. Source Sampling and Measurements

According to Nisbet and Sarofim[138] possible routes of PCB entrance into the environment include leaks and spills from sealed equipment, losses in manufacture, vaporization or leaking from PCB formulations and waste disposal of PCB and PCB containing products. Incineration of waste is probably the only route which presents a configuration convenient for making direct, in-stack source emission measurements. For diffuse sources such as open dump burning, accurate emission data are virtually impossible to obtain. The usual practice is to use ambient sampling and analytical procedures in the vicinity of the source and to apply estimates of thermal and turbulent diffusion, deposition, etc. to derive an approximate emission rate.

No data are available on the amount of PCB that escapes into the atmosphere with combustion products from municipal and commercial incinerators. Monsanto reports that PCB may be completely destroyed when incinerated at 800°C for 10 seconds and it has been postulated that municipal incinerators would not be a major source. Nevertheless, no data are currently available to confirm this and it is possible that poorly operated industrial and municipal incinerator may be significant sources of emission. Often hearth incinerators do not provide the preferred form of incineration due to possible vaporization of PCB on the drying grate and by-passing the flame zone in units where adequate mixing is not provided.

The possible formation of highly toxic chlorinated dibenzofurans (CBDF) and dibenzo-dioxines in the burning of waste containing chlorinated phenols and PCB should be investigated. Vos, et. al[6] suggest that the

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purification of PCB by a procedure involving blowing oxygen through the heated product may be the source of the extremely toxic CBDF found in some of the manufactured products. Current chemical techniques are not sufficiently sensitive to detect quantities that might be environmentally significant (sub nanogram or even sub picogram). Attempts should be made to determine if detectable amounts of the chlorinated dibenzofurans or dibenzodioxines are present at burning sources where there is a potential for incomplete pyrolysis and there are relatively rich levels of PCB or chlorinated phenyl in the refuse.

Although source sampling measurements on PCB have not been reported, sampling systems for detecting pesticides have been used. Stanley, et. al. (139) used a sampling train composed of a glass filter, a Greenburg-Smith impinger containing hexglene glycol and an adsorbent tube filled with alumina to detect various pesticides. The distribution of the pesticide through the three components was determined. At higher concentrations (417 ng/m^3), the per cent on the filter was highest. At lower concentrations the distribution was spread more evenly throughout the train. Caution should be exercised before reaching conclusions regarding the form of the pesticide based on the component on which it is collected. Collection efficiency studies by Miles et. al.[140] revealed that large retention percentages were found when vaporous pesticides were passed through glass, paper or membrane filters.

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