19 November 1975

Session II:

USES, SOURCES, AND IDENTIFICATION

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Session Chairman

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MONS 063744

INTRODUCTORY REMARKS

David Garrett

This session will deal with the uses, sources, and identification of PCB's, their disposal, reclaiming, and their treatment. All of us here on the podium have been required many times to share or contribute to many meetings involving discussions on PCB problems, and we are on a day-to-day basis directly involved with these problems.

Since discovery and commercialization of these substances with such marvelous commercial properties for which there appears to be no universally perfect substitute, some 500 million pounds have been pumped into our environment. Over this period after some 45 years, considering the PCB's still in service, the quantities destroyed via incineration, and natural dissipative forces, estimates have been given that some 125 to 135 million pounds are still available for biological activities.

Our eminent speakers will address both the quantities and active service life and the quantities still available for biological activity.

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CHARACTERIZATION OF POLYCHLORINATED BIPHENYLS

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Abstract

Assessment of the environmental impact of PCB products cannot be carried out without a basic understanding of the physical and chemical properties of these mixtures. PCB structure and nomenclature and the approximate composition of Aroclor products are presented. Several physiochemical properties which affect the performance and environmental impact of current dielectric products are described.

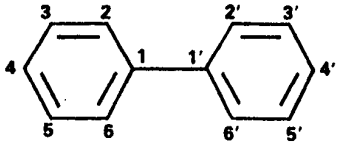
CHEMICAL STRUCTURE

Polychlorinated biphenyls (PCB's) are made by direct chlorination of biphenyl. The biphenyl molecule has 10 possible sites at which chlorine atoms can be substituted. The numbering system for the biphenyl structure is shown in figure 1. By convention, the two rings are numbered identically, except the ring with the fewest chlorine substituents or substituted in the highest numerical positions is designated as primed. Examples of nomenclature for a tri- and a tetrachlorobiphenyl are included in figure 1. An excellent discussion of PCB nomenclature can be found in a recent text by Hutzinger, Safe, and Zitko (ref. 1).

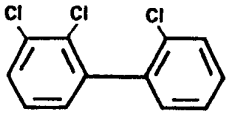
There are 209 possible chlorobiphenyl isomers distributed as indicated in table 1. However, many of these isomers are not likely to occur at significant levels in commercial PCB mixtures. For example, isomers with four or five chlorine atoms on one ring but none on the other ring are not detectable in PCB products.

AROCLOR PRODUCTS

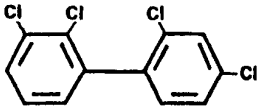
The major producer of PCB's in the United States is Monsanto Company, which markets mixtures for closed electrical system applications under the Aroclor trademark. Aroclor products are identified by a four-digit numbering code in which the first two digits, 12, indicate the parent molecule is biphenyl and the last two digits specify the weight percent of chlorine. The exception is Monsanto's newest product, Aroclor 1016 (41% chlorine), which retained the 1016 designation by which it was known during development. Aroclor products manufactured in the United States are listed in table 2.



BIPHENYL



2,2',3-TRICHLOROBIPHENYL



2,2',3,4'-TETRACHLOROBIPHENYL

Figure 1. The numbering system for the biphenyl structure.

Production of the materials listed as discontinued was terminated in or prior to 1971.

AROCLOR COMPOSITION

The composition of the four Aroclor products currently marketed in the United States is given in table 3. Aroclor 1221 is primarily monochlorobiphenyl while Aroclor 1016 and Aroclor 1242 are primarily trichlorobiphenyls. The major difference between these two products is the lower penta- and hexachlorobiphenyl

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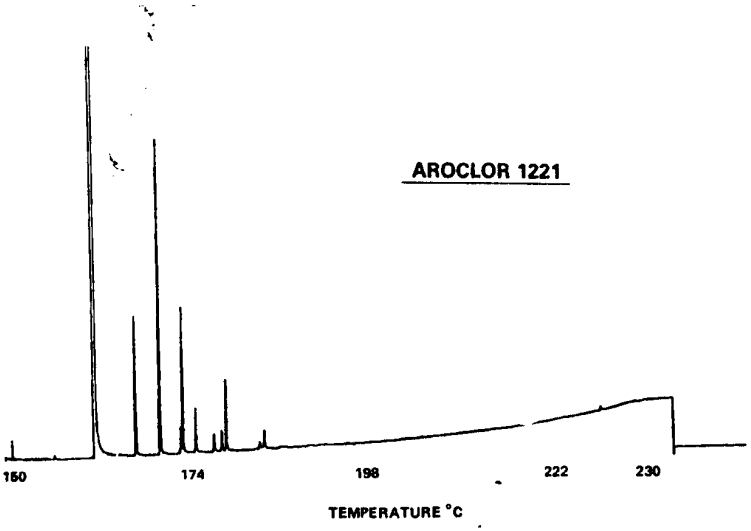

Figure 2. Detailed chromatogram of Aroclor 1221.

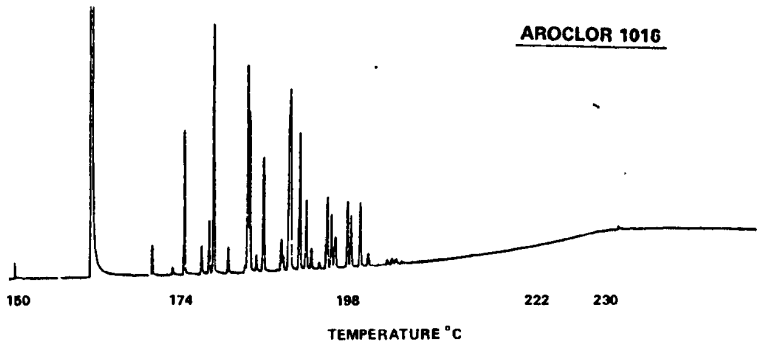

Figure 3. Detailed chromatogram of Aroclor 1016.

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Table 1: 209 possible PCB isomers

Degree of substitution	Number of isomers
Mono	3
Di	12
Tri	24
Tetra	42
Penta	46
Hexa	42
Hepta	24
Octa	12
Nona	3
Deca	1
	209

Table 2. Aroclor products manufactured in the United States

Current	Discontinued	Percent chlorine
1221		21
	1232	32
1016		41
1242		42
	1248	48
1254		54
	1260	60
	1262	62
	1268	68

content of Aroclor 1016. Aroclor 1254 is primarily pentachlorobiphenyl. The values in table 3 were calculated from measurements by gas chromatography with flame ionization detection after component identification by gas chromatography/mass spectrometry. All gas chromatographic separations were made with a high-resolution capillary column. Average response factors determined for each degree of chlorine substitution were applied to all components.

Detailed chromatograms of these four products are illustrated in figures 2-5. Specific isomer identifications determined by Webb and McCall (ref. 2) and Sissons and Welti (ref. 3) are listed for the major Aroclor 1242 components in figure 4. The complexity of these mixtures was emphasized by amplifying the first and last portions of the Aroclor 1254 chromatogram in figure 5. Eighty-five components were detected in Aroclor 1254. A .32-mm id x 50-m glass capillary column coated with OV-101 was used for these separations. The flow rate was 2 ml/min helium and the column temperature was programmed from 150° to 230° C at 2° C/min.

High-resolution chromatographic conditions are very useful for characterizing PCB products. However, for routine monitoring of environmental materials, it is more appropriate to use gas chromatography with packed columns and electron capture detection. Typical chromatograms of this type for Aroclor 1016 and Aroclor 1242 are compared in figure 6. The chromatograms are essentially identical for retention times less than 70 relative to p,p'-DDE. However, the higher chlorinated components with relative retention times 70 and greater represent a significantly smaller contribution in the Aroclor 1016 chromatogram. These chromatograms illustrate the feasibility of distinguishing these unaltered products. However, in environmental materials the characteristic features of Aroclor 1242 are frequently obscured by interfering compounds or by component alteration so the distinction is less clear or sometimes entirely lacking. These separations were carried out on a 6 ft x 4-mm id glass column packed with 3 percent SE-30 on 80/100 mesh Chromosorb W-HP at 190° C.

PHYSICOCHEMICAL DIFFERENCES

The physical and chemical properties of PCB isomers and commercial mixtures vary greatly depending on the degree and position of chlorine substitution. The effect of chlorine content on several physicochemical properties is summarized in table 4. Three of these properties, volatility, water solubility, and biodegradability, are very relevant to the environmental occurrence of PCB's. Volatility and water solubility represent potential mechanisms for introduction into and transport within the ecosystem. Biodegradation represents a mechanism for removing PCB's from the environment. Illustrations of the relative significance of these properties for different PCB isomers are evident from the following three examples.

Relative volatilities for the PCB components in Aroclor 1016 are indicated in figure 7 by comparing chromatograms of liquid and vapor composition. The higher

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Table 3. Typical percent composition of Aroclor products

Homolog # Cl/biphenyl	Aroclor 1221	Aroclor 1016	Aroclor 1242	Aroclor 1254
0	11	0.1	0.1	0.1
1	51	1	1	0.1
2	32	20	16	0.5
3	4	57	49	1
4	2	21	25	21
5	0.5	1	8	48
6	ND[a]	0.1	1	23
7	ND	ND	0.1	6
8	ND	ND	ND	ND

[a]ND = none detected, 0.01 percent.

Table 4. Physiochemical properties for PCB products

Property	Percent chlorine 21	42	54
Density (g/ml)	1.19	1.39	1.50
Distillation range (°C)	275-320	325-366	365-390
Fire point (°C)	176	None	None
Vaporization rate (mg/cm^2/hr @100 ° C)	1.74	.338	.053
Water solubility (ppm)	>.2	.2	.04
Biodegradability[a]	81	26	15

[a]Percent degradation/48 hr cycle with semicontinuous activated sludge.

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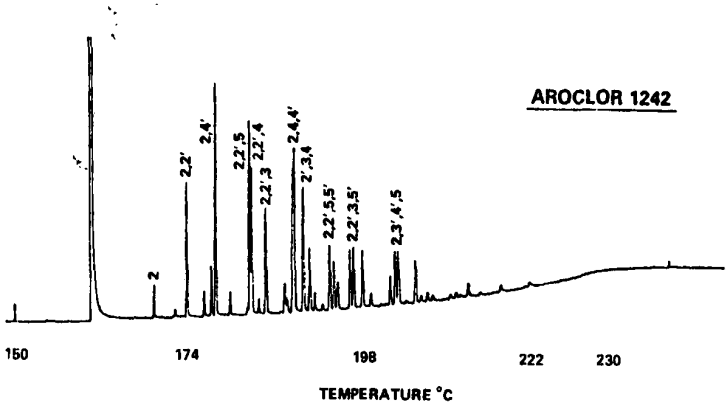

Figure 4. Detailed chromatogram and isomer identification--Aroclor 1242.

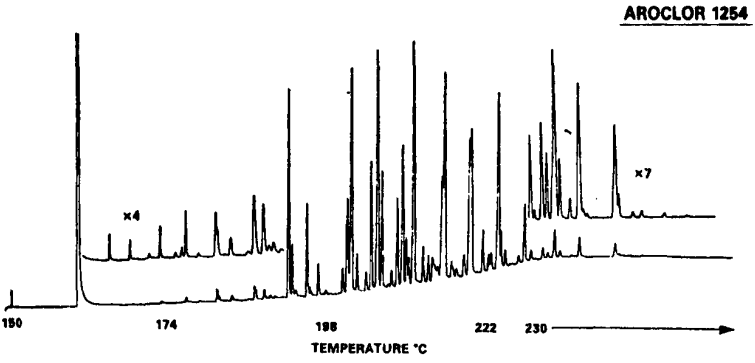

Figure 5. Detailed chromatogram of Aroclor 1254.

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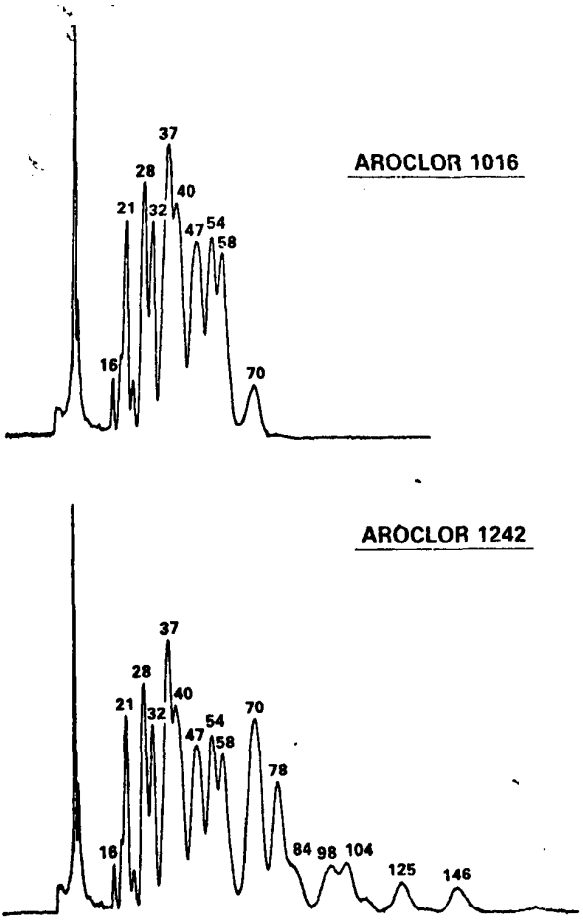

Figure 6. Comparison of electron capture chromatograms of Aroclor 1016 and Aroclor 1242.

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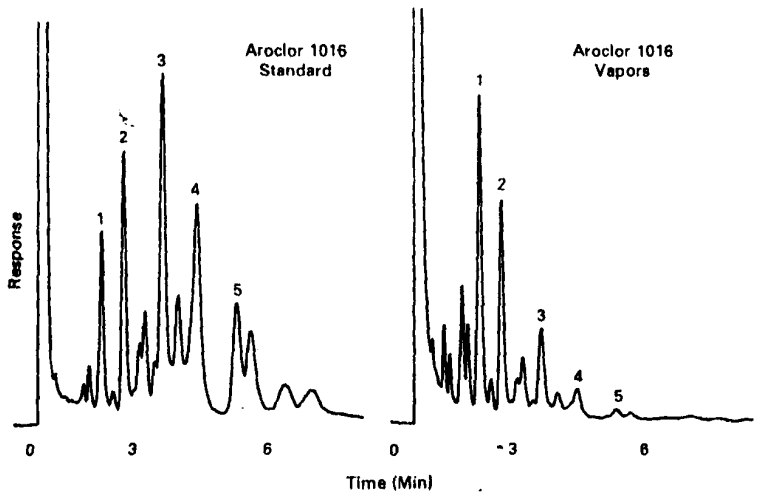

Figure 7. Relative volatilities for PCB components in Aroclor 1016.

numbered components make successively less contribution to the total vapor composition.

Water solubility of Aroclor 1016 components is illustrated in similar fashion in figure 8. Water saturated with Aroclor 1016 was extracted with hexane and the extract compared chromatographically to an Aroclor 1016 standard. The numbers above significant peaks express the percentage contribution of that peak area to the total area. Earlier eluting, lower chlorinated components are more soluble and contribute more to the water saturated composition. A related study has shown that PCB's leaching from Aroclor 1016 impregnated soils after the equivalent of 40 years annual rainfall consist of lower chlorinated biphenyls (ref. 4) (figure 9).

Microbial degradation also affects PCB isomers to different degrees. For example, figure 10 shows chromatograms depicting Aroclor 1016 composition after exposure to a naturally occurring mixed microbial population for 1/2 hour (above) and 14 days (below). The number above each GC peak indicates the percent biodegradation for that component. These percentages range from 17 to >98 and in general are higher for lower chlorobiphenyls. The exposure was carried out with activated sludge from a domestic sewage treatment facility. The sludge was previously acclimated to a mixture of industrial organic compounds before addition of 3 ppm Aroclor 1016. PCB composition was determined by extracting a representative aliquot of mixed liquor with hexane followed by analysis by gas chromatography using a glass capillary column and electron capture detection.

It is apparent from these examples that introduction of PCB's into the ecosystem by volatility or water solubility would enhance the ratio of lower to higher chlorinated biphenyls in the environment. PCB removal from the environment by either of these mechanisms or by microbial degradation would reduce this ratio. These and related factors combine to make assessment of PCB environmental impact a very complex problem.

In view of the recognized complexity in studying commercial PCB mixtures, it would seem expedient to substitute for the mixture a single isomer product having

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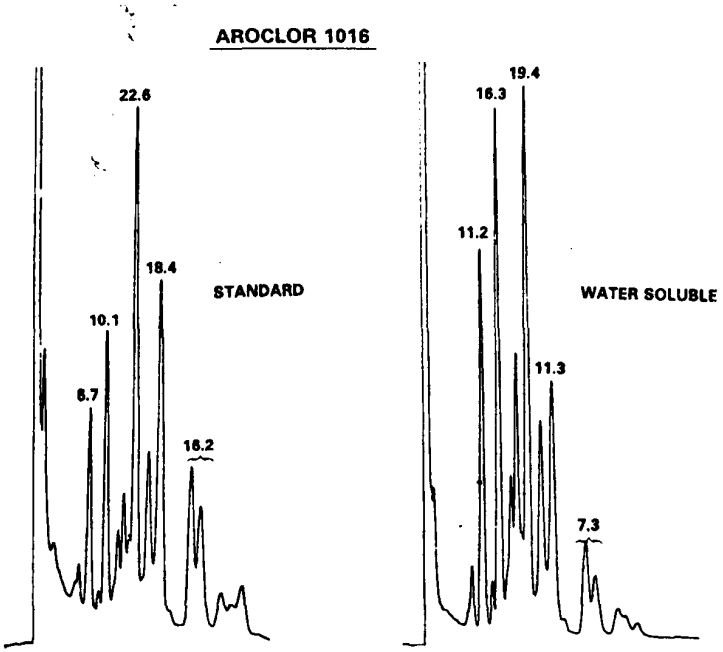

Figure 8. Water solubility of Aroclor 1016 components.

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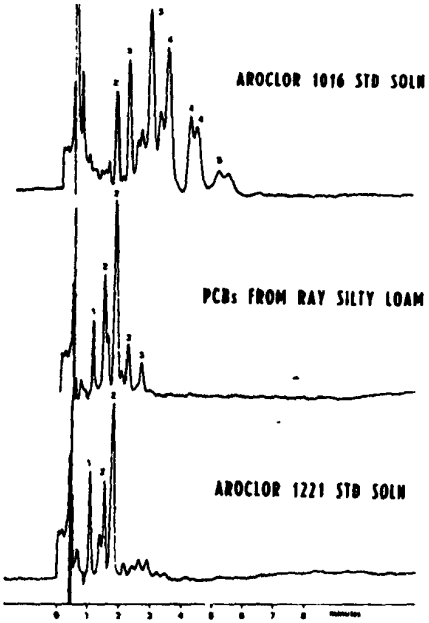

Figure 9. Composition of PCB's leaching from Aroclor 1016 impregnated soil.

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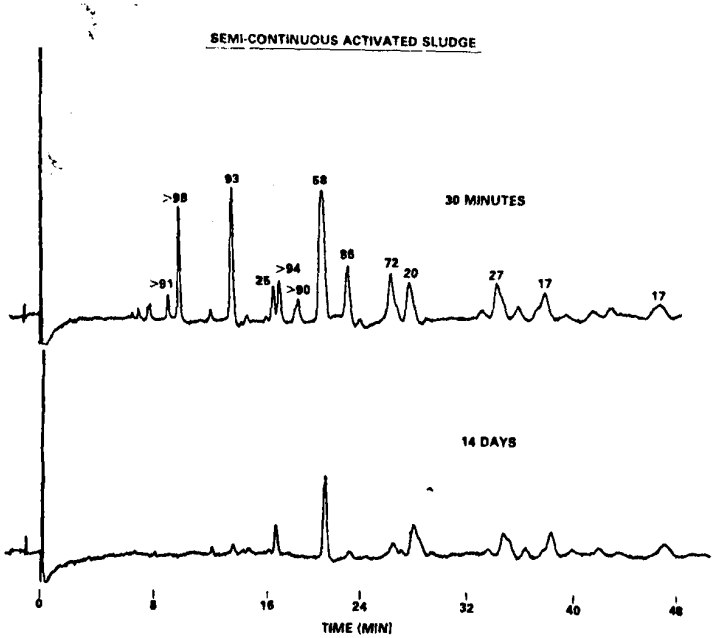

Figure 10. Aroclor 1016 biodegradation.

the desired electrical and physical properties. The environmental properties of this isomer would be much simpler to characterize and control. However, no such PCB isomer exists. Most PCB isomers are solid crystalline materials when isolated at 25° C. Commercial products are liquids only because of the mutual melting point depression exerted by the PCB components of the mixture.

CONCLUSIONS

Commercial PCB products are mixtures of many different isomers with varying chlorine content. The properties of these isomers, and hence the products, are vastly different and are complex to study. The environmental impact for each product must be accurately assessed and compared to the functional benefit.

REFERENCES

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4. E. S. Tucker, W. J. Litschgi, and W. M. Mees, *Bull. Environ. Contam. Toxicol.*, Vol. 13 (1975), p. 86.

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OVERVIEW OF ANALYTICAL IDENTIFICATION AND SPECTROSCOPIC PROPERTIES

Stephen Safe, Ph.D.*

Abstract

The analytical problems associated with PCB analysis involve many factors including sampling techniques, extraction and cleanup procedures, quantitation of PCB, confirmation of structure, and identification of metabolites and impurities. Recent studies in these areas of PCB analysis will be discussed and examples given.

Polychlorinated biphenyls (PCB) are among the most persistent and widespread environmental pollutants. Commercial PCB formulations can consist of up to 100 different chlorobiphenyl isomers and this is a complicating factor in the conventional gas chromatographic analysis of environmental samples. The chemical stability of PCB does, however, facilitate their analysis in that a variety of cleanup procedures can be used to remove coextractive material without modification of the PCB. The determination of PCB has been described in detail (ref. 1) and therefore most of the data and results reported herein will be associated with more recent publications.

The analytical problems associated with PCB analysis can be summarized under six major headings, which will be discussed in detail:

1. Sampling methods,
2. Extraction of PCB from environmental samples,
3. Cleanup procedures,
4. Quantitation of PCB levels,
5. Confirmation of structure, and
6. Identification of toxic impurities and metabolites.

1. *Sampling Methods*

PCB analysis is primarily concerned with determination of the pollutant concentrations in biological, sediment (or solid), water, and air samples. Specific sampling methods are required.

a. Biological samples and sediments. The sampling must insure that sufficient material is collected and extracted so that the analytical data obtained are representative of the sample.

b. Water samples. The sampling of water is complicated by the need to distinguish between dissolved PCB, which are usually low, and PCB adsorbed on particulate matter. The separation of the two fractions can usually be obtained using suitable filtration or centrifugation techniques (ref. 1).

c. Air samples. Air samples are usually obtained by passage of a known volume of air through an impinger or a similar device in which a suitable solvent preferentially extracts or removes airborne PCB (refs. 2,3).

2. *Extraction of PCB from Environmental Samples*

a. Biological samples. A number of methods have been described for the semiquantitative extraction of PCB from biological samples (e.g., > 90 percent recovery) (ref. 1). The sample can be macerated then freeze-dried, or dehydrated and extracted directly or by the soxhlet technique using an appropriate solvent. The choice of solvents can vary from nonpolar hexane or pentane to the more polar chloroform, acetone, or methanol. The more polar water-soluble solvents are useful in the extraction of wet tissue; however, the polar aqueous extracts are usually diluted with water and extracted with hexane to preferentially remove the nonpolar chlorinated aromatics. This partitioning technique is also utilized as a cleanup procedure to remove polar coextractives.

b. Sediments. Sediments and other solid samples are usually extracted with more polar solvents and ultimately the PCB are partitioned as described above (ref. 1).

c. Water. The simplest approach with water is by direct extraction with hexane. The removal of PCB from water has also been effected using polyurethane foam plugs and resins (refs. 4-6). Using this technique, the water is passed through a column containing the solid support and the PCB are adsorbed on these supports. Subsequent passage of a polar organic solvent through the columns removes the adsorbed organics, which can be further cleaned up using the partitioning technique.

d. Air. PCB are readily extracted from air by passage of the air through sintered glass funnels or suitably contracted glass impingers filled with solvents (e.g., amyl acetate, sec-butanol or ethylene glycol) (refs. 2,3). The PCB can then be isolated by the standard partitioning technique.

3. *Cleanup Procedures*

The major aim of a cleanup procedure is to selectively remove coextractive natural material and xenobiotics from an extract containing PCB. Solvent partitioning has already been discussed and is an excellent

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method for removing water-soluble and highly polar co-extractive organics. The two additional important cleanup techniques are methods based on column or thin-layer chromatography and chemical treatment of the extract to modify either the PCB or the coextractives.

a. Chromatographic methods. Most chromatographic procedures include column chromatography on activated florisil and/or alumina using hexane to elute the PCB (refs. 7,8). Thin-layer chromatography with silicic acid and alumina can also be used. An example of a typical chromatographic cleanup procedure is outlined in figure 1.

b. Chemical methods. Since PCB are thermally and chemically stable, it is possible to saponify extracts by both acidic and basic treatment without altering the PCB. This procedure is particularly useful in the conversion of lipid esters, which have chromatographic properties similar to PCB, into more polar products. One of the major problems in PCB cleanup is to remove DDE, which has similar chromatographic properties to PCB. A recent paper describes an oxidative technique which quantitatively converts DDT, DDE, and their analogs into more polar products (ref. 9). Dehydrochlorination with mild base converts DDT and DDT-like compounds into the corresponding bisdiarylethylenes (e.g., DDE); treatment of the olefin with chromic acid gives the corresponding benzophenones, which are readily separated from PCB. The PCB are not affected by this chemical modification procedure. Raney nickel reduction and sulfuric acid treatment of crude PCB extracts are also useful in the cleanup of river water extracts (ref. 10).

The analysis of PCB is always complicated by the large number of isomeric chlorobiphenyls that are present and this results in a complicated gas chromatogram even after cleanup (figure 2). In addition, polychlorinated terphenyls (PCT) and polychlorinated naphthalenes (PCN) are also industrial environmental pollutants which are composed of several isomeric components that can co-occur with PCB. A perchlorination procedure was reported in which the isomeric mixtures can be converted into their respective perchloro derivatives (refs. 11,12), as shown in figure 3. These compounds can then be readily analyzed and quantitated by conventional gas chromatography (figure 2). The comparative gas chromatographic retention times of several perchlorinated pollutants are: decachlorobiphenyl, 1.0; octachlorodibenzofuran, 2.55; octachlorodibenzo-*p*-dioxin, 2.80; dodecachloro-DDE, several peaks > 1.9; tetradecachloro-*o*-terphenyl, 11.9; tetradecachloro-*m*-terphenyl, 19.2; tetradecachloro-*p*-terphenyl, 22.2.

It should be noted that this procedure is markedly dependent on the purity and source of the commercial antimony pentachloride reagent and the composition or degree of chlorination of the PCB. A drawback of this

General Cleanup Procedure

(suitable for most air, water, biological and sediment analyses)

Crude Extract	Rationale
↓ solvent partition (hexane: polar solvent)	polar imputities remain in polar solvent
hexane extract	
↓ chromatography on activated alumna	Removal of nonpolar lipids, impurities, and some chlorinated pollutants
purified PCB	
↓ chromatography on activated silica gel	Removal of nonpolar lipids and separation of PCB from DDT and its metabolites
purified PCB	

Figure 1. General cleanup procedure.

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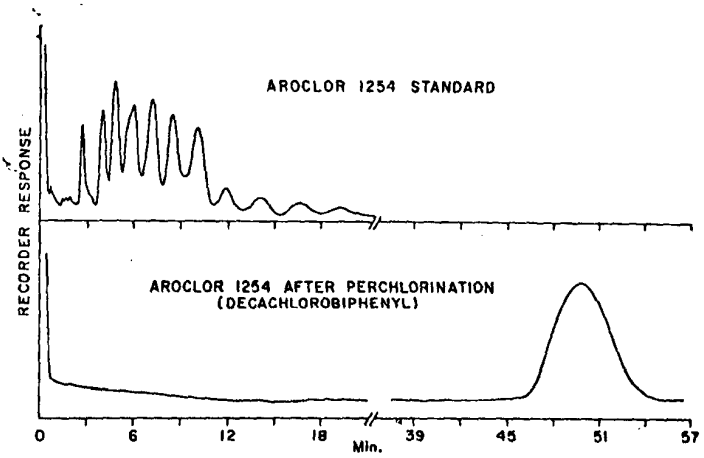

Figure 2. Gas chromatogram after cleanup.

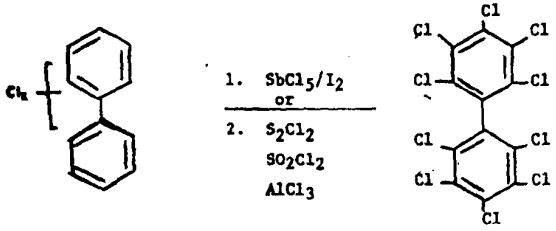

Figure 3. Perchlorination procedure in which isomeric mixtures can be converted into their respective perchloroderivatives.

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technique is the reported formation of varying quantities of a sideproduct which has been identified as bromo nonachlorobiphenyl (refs. 13,14). This introduces a second peak which is observed in the gas chromatogram and this side reaction can also reduce the overall yield of the decachlorobiphenyl product.

4. *Quantitation of PCB*

Gas chromatography is the method of choice for PCB analysis and electron-capture detection is by far the most sensitive procedure for detecting these chlorinated aromatic compounds (ref. 1). A comparison of the relative molar responses of electron-capture and flame-ionization detector to some isomeric chlorobiphenyls is given in table 1. It is evident that the electron capture detector is the more sensitive and that the relative molar response is both a function of the degree of chlorination and the position of the substituent (refs. 15,16). Since the precise composition of PCB mixtures is not known, the quantitation of the complex chromatograms can only be an estimated value. A more consistently accurate method would involve perchlorination since the relative molar response and chromatographic properties of decachlorobiphenyl are known. Quantitation of the PCB mixtures is usually obtained by measuring the total peak heights or areas of key diagnostic peaks that are present in the environmental PCB extract and comparing this result with the heights or areas obtained in the gas chromatogram of the appropriate commercial PCB mixture (e.g., Aroclor 1254, Clophen A-60). An example is shown in figure 4, in which the chromatograms of Clophen A-60 and river water extracts are compared and the quantitation is carried out using three diagnostic peaks present in the environmental and commercial PCB sample (ref. 10).

5. *Confirmation of Structure*

PCB in the environment was originally detected by gas chromatography and later confirmed by mass spectrometry and this technique is the most sensitive and

Table 1. Relative molar responses of electron-capture and flame-ionization detectors to some chlorobiphenyls

Chlorobiphenyl	Relative molar response	
	Electron capture	Flame ionization
2-	1.00	1.00
3-	0.20	0.92
4-	1.10	0.87
2,2'-di	5.16	0.99
2,4'-di	17.7	0.86
2,6-di	32.0	0.91
3,3'-di	6.10	0.94
3,4-di	15.2	0.86
4,4'-di	5.97	0.81
2,4,4'-tri	135	0.78
2,2',4,4'-tetra	106	0.87
2,2',6,6'-tetra	20.6	0.90
3,3',4,4'-tetra	396	0.87
3,3',5,5'-tetra	320	0.85
2,3,4,5-tetra	367	0.87
2,3,5,6-tetra	259	0.71
2,2',4,4',6,6'-hexa	347	
3,3',4,4',5,5'-hexa	726	
2,2',3,3',4,4',6,6'-octa	1180	
2,2',3,3',5,5',6,6'-octa deca	1150 1410	

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Quantitation of PCB

1. The method of choice is gas chromatography (GC) using an electron capture (EC) detector. The major problem is selecting suitable standard peaks to use as quantitative standards for comparison with the commercial PCB standard samples.

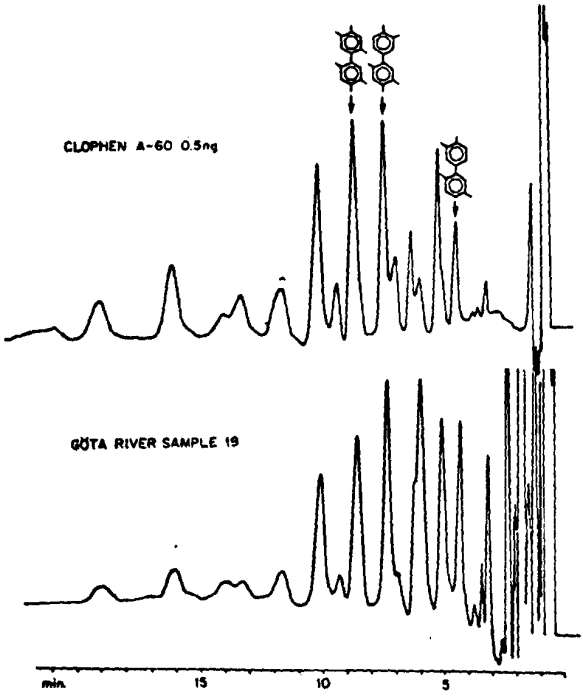

Figure 4. Gas chromatographic analysis with electron capture detector. The injected volume of river water extract corresponds to 1.6 liters water.

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widely used spectroscopic method for the confirmation of PCB. The mass spectrometry of isomeric chlorobiphenyls and the applications of this technique in environmental analysis has been reviewed (ref. 17) and only recent applications of this analytical technique will be mentioned.

a. Gas chromatography – mass spectrometry (GC-MS). Gas chromatographic analysis of PCB can be carried out by combination GC-MS so that the mass spectrum of the individual peaks which elute from the gas chromatograph can be recorded. This technique in combination with a computer has been extensively used in environmental analysis for both the detection and confirmation of environmental PCB, related metabolites, and toxic impurities (refs. 1,17). A GC-MS of an environmental sample may generate hundreds of spectra; however, using the computer the analyst can recall individual spectra as well as conduct limited mass searches on key diagnostic ions.

b. Mass fragmentography GC-MS (ref. 18). The mass spectrum of a sample is obtained by scanning the entire mass range in order to record all the ions that are generated. If a mass range of 400 is scanned in a period of 4 seconds, then the mass spectrum is held for only 1/100th of a second at each mass unit; for the remaining 3,99 seconds the ion current at that mass value is lost. Mass fragmentography is a technique which simultaneously monitors the ion current at one or more mass values for the complete duration of the sample spectrum (i.e., for 4 seconds rather than 0.01 second). The mass values which are monitored are the most intense and diagnostic ions generated by a compound. For PCB this is usually the isotopic molecular ion species or the isotopic M-Cl^2 ions. The sensitivity of a GC-MS instrument operating in the mass fragmentography mode can surpass that of an electron capture detector. An example of this technique is shown in figure 5, in which the mass fragmentograms of standard Clophen A-60 and river water

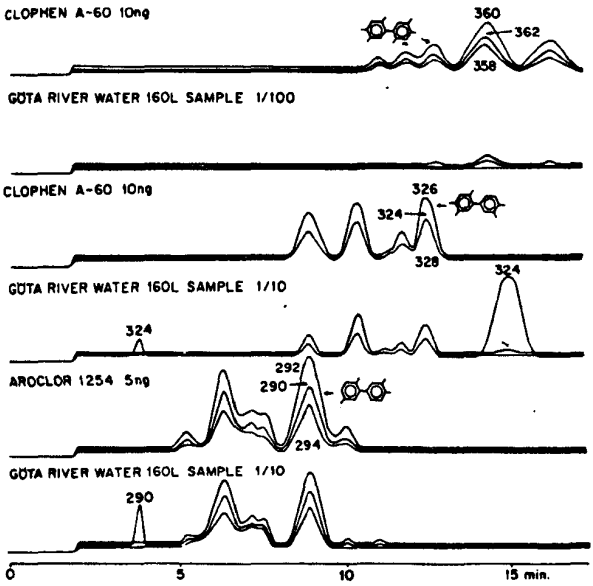

Figure 5. Mass fragmentograms of PCB Standards and river water extracts.

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extracts are compared (ref. 19). The diagnostic ions which were used are the isotopic hexachlorobiphenyl (m/e 362, 360, and 358), pentachlorobiphenyl (m/e 328, 326, and 324), and tetrachlorobiphenyl (m/e 294, 292, and 290) molecular ions.

c. High-resolution photoplate mass spectrometry. The relatively large mass deficiencies of both chlorine isotopes cause the exact masses of ions which contain chlorine to be usually less than ions of the same nominal mass that contain only isotopes of C, H, N, and O (see table 2). Thus, a typical lipid coextractive would appear at mass positive integer values whereas the molecular ion for a tetrachlorobiphenyl isomer (accurate mass 289.9224) appears at 776 millimass units below the integer value. Mass negative PCB ions are therefore readily distinguished from mass positive ions which occur at the same nominal mass by high-resolution techniques. A photographic plate can be used as an integrating ion detector and the subsequent identification of the PCB on the plates is readily carried out. This technique has been used in the detection of PCB in biological samples as well as confirming the presence of hydroxylated PCB metabolites (refs. 20,21).

6. *Identification of Toxic Impurities and PCB Metabolites*

Analysis of commercial PCB preparations showed that higher chlorinated naphthalene isomers were present as trace impurities and their structures were confirmed by mass spectrometry (ref. 22). More recently the highly toxic chlorinated dibenzofurans have also been identified in commercial preparations; the flow chart in figure 6 outlines chromatographic procedures for the isolation of these components (ref. 23).

The metabolism of PCB in diverse animal and microbial systems has been investigated and the results indicate the conversion of these substrates into a range of hydroxylated metabolites (ref. 24). Figure 7 summarizes a composite scheme for the separation and identification of PCB metabolites and it should be noted that all the steps are used in the cleanup procedure only when it is necessary. Recent data from seal extracts has confirmed the presence of hydroxylated PCB in their fatty tissue (ref. 25). These metabolites are therefore a new class of chlorinated aromatic pollutants derived from PCB.

The financial support of Environment Canada is gratefully acknowledged.

Table 2. Confirmation of PCB by high-resolution phosphate MS

Basic principles: Xenobiotics containing mass deficient atoms (e.g., Cl) appear at lower mass values than most "natural coextractives"; these differences can be measured using the above technique.

Atom or compound	Accurate mass	Deviation from integer value (in millimass units)
^{12}C	12.000	-
^{1}H	1.0078	+78
^{14}N	14.0031	+31
^{16}O	15.9949	-51
^{35}Cl	34.9688	-312
^{37}Cl	36.9659	-341
Lipid coextractive	variable	

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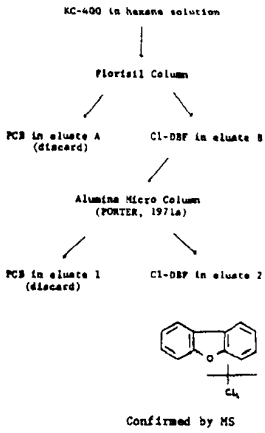

Figure 6. Procedure for separation of chlorinated dibenzofurans from chlorinated biphenyls in KC-400.

Laboratory experiments show that PCB isomers are metabolized to hydroxylated PCB which can be isolated and identified as indicated.

Urine Sample	Rationale
↓ strong acid hydrolysis and ether extraction	Hydrolysis of glucuronides
Ethereal Extract	
↓ further cleanup via base extraction of phenols (optional)	Separation of phenolic from other coextractives
Crude Hydroxy PCB	
↓ TLC, then extraction of "Hydroxy Band"	
"Hydroxy Band"	
↓ formation of acetate or methoxy derivative than TLC, and hydrolysis (optional)	Structures proven by M.S. and NMR spectra and by synthesis[1-4]
Purified Hydroxy PCB	

Figure 7. A composite scheme for the separation and identification of PCB metabolites.

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PRODUCTION AND USAGE OF PCB's IN THE UNITED STATES

Robert L. Durfee, Ph.D.*

Abstract

About 99 percent of the PCB's used in U.S. industry are produced by Monsanto in a single facility at Sauget, Illinois. These materials, termed Aroclors, are used in the production of capacitors (70 percent) and transformers (30 percent). Imported PCB's, comprising slightly over 1 percent of U.S. usage, are used in investment casting operations (80 to 90 percent; decachlorobiphenyl) and semiclosed heat transfer applications (10 to 20 percent). Capacitor and transformer production processes are similar in that process steps involving PCB's include filtration, flood or individual filling of the products, and removal of excess PCB's prior to sealing and individual testing of the products. Most losses occur from pump leaks to cooling water, spills, personal hygiene practice, and the like. Many of the discharges containing PCB's are to municipal sewers.

Introduction

Polychlorinated biphenyls (PCB's) represent a class of compounds produced commercially by the chlorination of biphenyl. Most PCB's currently used in the United States are mixtures of chlorobiphenyls containing up to seven chlorine atoms per molecule, although some decachlorobiphenyl (10 chlorines per molecule) is imported. The production and the types of uses for PCB's increased steadily from initiation of production in 1929 until industry-imposed restrictions in 1971 curtailed production and essentially eliminated use of domestic production in all but "closed" electrical equipment (specifically, capacitors and transformers).

PCB's have been increasingly identified as a significant environmental pollutant. In our work for the Office of Toxic Substances, Versar is studying the economics and other aspects of possible regulatory alternatives as applied to PCB's. We are also studying treatment methods which might be applied to control of waterborne PCB's in industrial effluents. The purpose of this paper is to define current PCB production and use, including process technology and sources of wastes containing PCB's.

Domestic Production and Imports

Monsanto, the sole domestic manufacturer of PCB's, manufactures this chemical in its Sauget, Illinois, plant. The basic raw material is biphenyl, which is manufactured from pure benzene in another Monsanto plant. The PCB manufacturing operation is conducted in two steps. First biphenyl is chlorinated with anhydrous chlorine in presence of ferric chloride to produce crude PCB's and then the crude PCB's are distilled to obtain the finished product. A schematic flow diagram of this process is given in figures 1 and 2.

Monsanto currently produces Aroclors 1221, 1016, 1242, and 1254 (chlorine contents approximately 21, 41, 42, and 54 percent by weight, respectively). For the production of a given product, biphenyl and catalyst are heated to melting and chlorine gas is introduced while the charge is circulated with a pump. The time of chlorine contact controls the degree of product chlorination. Vapors from the chlorination (HCl) are scrubbed and removed to another part of the plant.

The crude product is held at temperature and blown with dry air for several hours, and then is sent to storage where a small amount of lime is added to remove remaining HCl or ferric chloride. The blown air is scrubbed and vented to the atmosphere through a demister.

Purification, as typified by figure 2, varies somewhat between the different products. The 1016 material is processed in a retort and a vacuum distillation (steam jet ejection) to remove the more highly chlorinated compounds. The first cut from the tower is recycled to the retort. When a preset overhead temperature is reached, the product is removed and sent to storage and shipment. The other Aroclors are vacuum distilled (steam jet ejectors), the product being the condensate. The still bottoms (called Mentars) are incinerated.

Monsanto's production in 1974 was 40,466,000 lb, of which 34,406,000 was sold domestically and 5,395,000 lb exported. Production has been about at the 40-million-pound level since 1971, and reached a high of 85 million pounds in 1970. Company expectations are for a sizeable increase in sales in 1976, followed by small, steady growth.

Imports in 1973 and 1974 amounted to 1.2 to 1.5 percent of Monsanto's domestic sales in those years. Importation appears to be steady or slightly increasing. The major source of imported PCB's is Italy, from which decachlorobiphenyl made by Caffaro is imported by one company for use in investment casting waxes. This constitutes 80 to 90 percent of the imports; the other 10 to 20 percent originates in France (Prodelec) and is used

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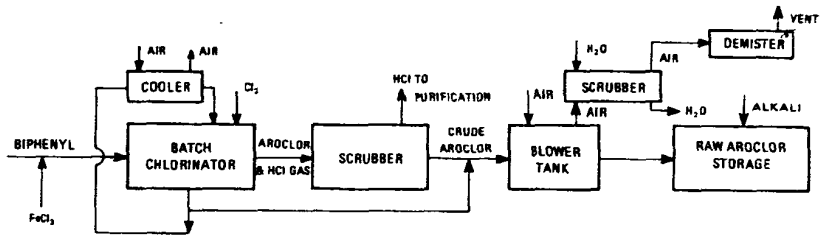

Figure 1. Preparation of crude chlorinated biphenyls Monsanto Krummrich plant.

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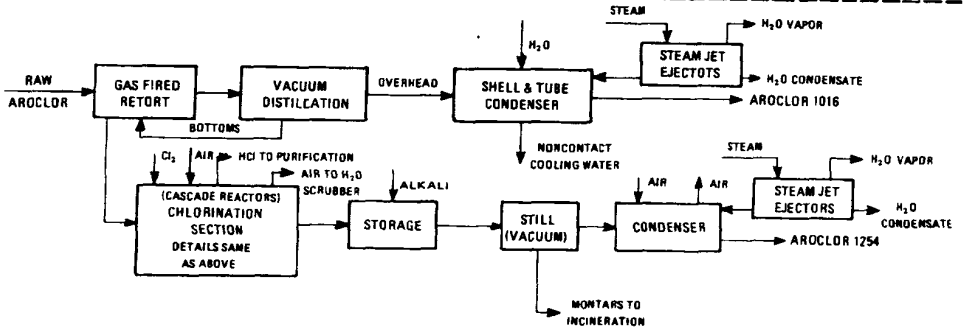

Figure 2. Distillation of crude products Monsanto Krummrich plant.

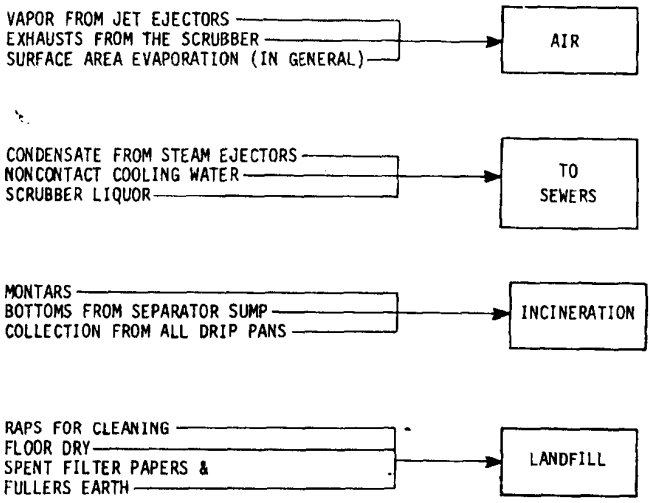

Figure 3. Nonproduct PCB discharges at Monsanto's Krummrich plant.

in semiclosed heat transfer applications. Until recently PCB's were used in some U.S. built mining machines, but this use has been discontinued.

In the Monsanto process, PCB's can be released to the environment through the sources listed on figure 3. Waterborne discharges of PCB's at this plant have been reduced greatly over the past few years, and are now below 1 pound per day, according to Monsanto.

Capacitor and Transformer Production

Producers of capacitors and transformers utilize essentially all of Monsanto's domestic sales of PCB's. About 70 percent of the usage is in capacitor production, and, of this total, roughly half is for small capacitors and half for large capacitors. Lists and locations of capacitor and transformer producers are presented in tables 1 and 2, respectively.

Transformers containing PCB's comprise only about 5 percent of the U.S. transformer market, and are used only where safety and reliability are of prime importance. On the other hand, about 95 percent of capacitors made in the United States utilize PCB's. According to General Electric, about 100×10^6 capacitors containing PCB's are made in the United States yearly, most for first-time use in products. Life expectancy for capacitors is over 10 years for lighting applications and over 20 years in electric utility service. Life expectancy of transformers containing PCB's is over 30 years, and some 135,000 have been put into service since 1932 (virtually all are still in service).

The steps involving PCB's used in the manufacture of capacitors and transformers include filtration of PCB's, filling (under vacuum), removal of excess PCB's, sealing of units, and heat and electrical testing. Sources of nonproduct discharges of PCB's are roughly similar for capacitor and transformer production plants, and are listed in table 3.

Most of the in-plant PCB wastes which reach water streams originate in the filling area. A brief description of the various filling processes is presented below.

Small capacitor bodies, each containing a machine-

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Table 1. U.S. transformer manufacturing industry using PCB's

Company name	Location of the plant
Westinghouse	South Boston, Va. Sharon, Pa.
General Electric Company	Rome, Ga. Pittsfield, Mass.
Research-Cottrell	Finderne, N.J.
Niagara Transformer Corp.	Buffalo, N.Y.
Standard Transformer Co.	Warren, Ohio Medford, Oreg.
Helena Corp.	Helena, Ala.
Hevi-Duty Electric	Goldsboro, N.C.
Kuhlman Electric Co.	Crystal Springs, Miss.
Electro Engineering Works	San Leandro, Calif.
R.E. Uptegraff Mfg. Co.	Scottsdale, Pa.
H.K. Porter	Belmont, Calif. Lynchburg, Va.
Van Tran Electric Co.	Vandalia, Ill. Waco, Tex.
Esco Manufacturing Co.	Greenville, Tex.

Table 2. U.S. capacitor manufacturing industry using PCB's

Company name (In order of PCB's usage)	Location of the plant
General Electric Company	Hudson Falls, N.Y. Ft. Edward, N.Y.
Aerovox	New Bedford, Mass.
Universal Manufacturing Corp.	Bridgeport, Conn. Totowa, N.J.
Westinghouse Electric Corp.	Bloomington, Ind.
Cornell Dubilier	New Bedford, Mass.
P.R. Mallory & Co., Inc.	Waynesboro, Tenn.
Sangamo Electric Co.	Pickens, S.C.
Sprague Electric Co.	North Adams, Mass.
Electric Utility Co.	LaSalle, Ill.
Capacitor Specialists, Inc.	Escondido, Calif.
JARD Corp.	Bennington, Vt.
York Electronics	Brooklyn, N.Y.
McGraw-Edison	Greenwood, S.C.
RF Interonics	Bayshore, L.I., N.Y.
Axel Electronic, Inc.	Jamaica, N.Y.
Tobe Deutschmann Labs.	Canton, Mass.
Cine-Chrome Lab, Inc.	Palo Alto, Calif.

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Table 3. Sources of nonproduct discharges of PCB's

Source	Type of effluent/ typical disposal
Vacuum pumps	Air
Evaporation and ventilation	Air
Transfer spillage	Water
Vacuum pump cooling water or condensate (steam jet)	Water
Personal hygiene	Water (Municipal Sewer)
Reject products	Landfill
Floor and equipment cleanup wastes	Landfill
Drip pan collection	Incineration
Filter media	Landfill

wrapped helix of alternating paper and aluminum foil, are placed in a chamber, the chamber is evacuated, and prefiltered dielectric oil is introduced until it covers the capacitors. The vacuum assures that the paper will be well soaked (impregnated) with the fluid.

After the filling operation the vacuum is released, excess fluid is removed to a holding tank, and the capacitors are sealed and then deoiled. Then they undergo heating electric tests and, if specifications are met, are packaged. Reject capacitors and, in many cases, solid wastes containing PCB's are landfilled.

Large capacitors are produced similarly, although some differences can be observed:

1. Large capacitors (over 2 to 3 lb of PCB's) are typically filled through a small fill hole, while the fill tank is under vacuum. Large capacitors may be filled separately or flood-filled in a chamber. Some plants use a multicell "carousel" arangement where loading and unloading occurs at one station, and the capacitor(s) in each cell are progressively dried, evacuated, filled, and the fluid drained from the cell at stations along the carousel.
2. Following the filling operation, the fill holes in the large capacitors are sealed or plugged with solder, deoiled, and then tested prior to packaging and shipment.

Transformer filling is very similar to the filling of the larger capacitors, but transformers are all filled individually. Individual filling appears to generate less waste PCB's from spills, drip, and deoiling operations. If a transformer does not meet test specifications, the fluid is drained, filtered, and returned to the supply tank, and the windings assembly and other parts are inspected to identify the cause. Once repaired, the transformer reenters the assembly line.

Investment Casting Process

Imported decachlorobiphenyl (deka) is used as a filler for investment casting waxes; the estimated yearly usage is about 400,000 lb, some of which is in exported waxes. In investment casting, a pattern is made of the wax and a ceramic mold is formed on the wax. The wax is melted out, and the mold, after baking out in a furnace, is ready for use. The wax used to form the pattern contains about 60 percent used wax and 40 percent virgin pattern wax. Significant losses of PCB's to the atmosphere can occur in the melting out process and in the furnace. Used wax can possibly be reclaimed, but most appears to be landfilled. Polychlorinated triphenyls are also used as pattern wax fillers.

MONS 063769

PCB DISPOSAL, RECLAIMING, AND TREATMENT

Thomas E. Kopp*

Abstract

The Environmental Protection Agency in 1975 sought information about the uses, disposal, and effects of PCB's from 84 purchasers and importers of PCB's. Responses indicate that while PCB's were formerly disposed of in landfills, high-temperature incineration is now prevalent. There is no proven technology for removal of PCB's from water, and emphasis is on preventing production-line PCB's from entering waste water. EPA is presently formulating criteria for ambient PCB levels in water and is developing a new toxic effluent standard.

On August 16, 1975, the Office of Enforcement, EPA, sent out 84 letters (figure 1) to companies in the United States that purchase PCB's from Monsanto, to those that import them, and to others that may be users. This letter has been modified to include polychlorinated terphenyls, PCT's, both because of their similar structure and because they are a type of chemical that we will have evaluated in the whole program of PCB's. This letter concluded with four pages of questions which covered the uses, importation, reclaiming, disposal of PCB's (figure 2) and which concerned effluents, transportation, spills, health and environmental effects, and other data the companies had on file (figure 3).

Since then, we have received 83 responses and we are in the process of evaluating and assembling the information into a useable form for making decisions within the Federal Government. This information will be made available to the public and to local and State governments. This information will be handled in accordance with the confidentiality requested by the companies and the Trade Secrets Act.

Starting in 1972, industry had developed a standard for handling and disposal of PCB's (figure 4). In 1974, this standard was finalized and published. It covers the following points (figure 5): housekeeping, disposal, effluents, analytical methods, and several other important areas. This is a voluntary standard for industry and for the Federal Government. We encourage the implementation of this standard support by everybody and also support the proposal by the National Electrical Manufacturers Association to revise and update it in the near future.

Disposal of PCB's has historically been to the local landfill site or to a scrap oil dealer. Since the concern with the environmental problems associated with PCB's has become evident, industry has developed several ways of disposing of its PCB waste (figure 6). High-temperature incineration is the most effective way we know today because it will completely destroy PCB's. The other methods are only to contain the material and not to let PCB's get out into the environment.

In Canada, there is a study going on about which we have little knowledge (figure 7). It appears to be a method by which PCB's may be reclaimed after their useful lives.

On Thursday, December 27, 1973, EPA issued its proposed toxic pollutant effluent standards under Section 307a of the Water Act. During the hearings in May, 1974, effluent treatment was discussed (figure 8). Westinghouse stated that "A review of techniques for removal of materials such as PCB's from the water has revealed that no commercial operation is now in effect. Furthermore, there is no proven technology on which such a technique might be based." General Electric stated that "The control of PCB's from current production is basically a containment process. Water is not an essential component of the manufacturing process, so the problem is not one of removing a contaminant from an aqueous process stream, but of preventing the adventitious loss of PCB's from the production line to a waste water line." Monsanto stated for its production facility that "the bathtub approach, which really involves paving, curbing, isolating the drains, ... etc.," is the only known method for treatment.

We are basically at the same place today as we were in May of 1974. As EPA develops its reproposed toxic effluent standard, which should be published the first half of next year, we will be looking at carbon absorbtion, reverse osmosis, and ozonation.

EPA is almost ready to send out for interagency and State review of the Criteria for Water Quality, Section 304a of the Water Act (figure 9). This is not a rule-making procedure so it does not have to go through hearings and rulings. This is the ambient level which we desire will not be exceeded in the Nation's waters.

There have been 20 spills identified at this time which have involved PCB's (figure 10). Only six of these were reported to EPA, and only over these did we have any control during the cleanup. There is only one out of

*Environmental Protection Agency, Office of Toxic Substances (WH-557), Washington, D.C.

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

AUG 16 1975

OFFICE OF ENFORCEMENT

Gentlemen:

Recent governmental sampling data indicate the presence of Polychlorinated Biphenyls (PCBs) and comparable chemical substances in the air, in water bodies, and in fish in several areas of the country. In order to determine the nature and extent of the possible adverse effects resulting from the presence of PCB compounds in the environment, the Environmental Protection Agency (EPA), in cooperation with other federal and State agencies, is attempting to determine the sources and amounts of PCBs entering the environment. It is important that this effort be carried out without delay.

It is our understanding that your company handles PCB compounds or mixtures or comparable chemical substances in its operations. I am therefore requesting, pursuant to the authority provided by Section 308 of the Federal Water Pollution Control Act, as amended, 33 U.S.C. 1318, and Section 114 of the Clean Air Act, as amended, 42 U.S.C. 1857c-9, that your company furnish EPA with information pertaining to your use and handling of PCBs and comparable chemical substances. In addition to a general description, which should include information as to sources, quantities, uses, and ultimate disposition, you should respond in detail to the enclosed questions. If any question is not applicable to your company or operations, please so indicate by responding "not applicable."

The information requested herein must be provided notwithstanding its possible characterization as confidential information or trade secrets. Should you so request, however, any information (other than effluent or emission data) which the Administrator of this Agency determines to constitute methods or processes entitled to protection as trade secrets will be maintained as confidential, pursuant to procedures specified in 40 CFR Part 2.

Figure 1. Letter from EPA to purchasers, importers, and users of PCB's.

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Within 14 days of receipt of this letter, your company must provide all information concerning your current status and activities and covering the twelve month period immediately preceding receipt of this letter.

Within 30 days following receipt of this letter, your company must provide all information for all of the prior years indicated.

The information required herein should be sent directly to the address indicated below. If you have any questions you may call the person indicated below or Mr. Blake A. Biles of our office at (202) 755-8731.

We appreciate your prompt cooperation in this matter.

Sincerely yours,

Stanley W. Legro
Assistant Administrator
for Enforcement

Enclosure

Regional Contact:
Mr. Richard O'Connell
Director, Enforcement Division
Environmental Protection Agency
100 California Street
San Francisco, California 94111
Telephone: (415) 556-0102

Figure 1. Letter from EPA to purchasers, importers, and users of PCB's (con.).

MONS 063772

POLYCHLORINATED BIPHENYL (PCB) COMPOUNDS OR MIXTURES

Within 14 days of receipt of this letter, your company must provide all information concerning your current status and activities and covering the twelve month period immediately preceding receipt of of this letter.

Within 30 days following receipt of this letter, your company must provide all information for all of the prior years indicated.

For purposes of this letter, the phrase "PCB compound or mixture" includes all chemical substances known or believed by you to be PCB compounds or mixtures or of a similar chemical nature, irrespective of trade name.

1. For each PCB compound or mixture produced or imported by your company, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. The total amount of each PCB compound or mixture produced or imported.

   b. The name and address of each of your company's facilities which handle PCB compounds or mixtures (including production facilities and wholesale and retail outlets), and the amount of each PCB compound or mixture distributed through each facility.

   c. The name and address of each customer of each PCB compound or mixture, and the amount of each PCB compound or mixture obtained by each customer from each facility.

2. For each PCB compound or mixture incorporated by your company into its products, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. A description of each product.

   b. For each product the total amount incorporated of each PCB compound or mixture.

2. (continued)

   c. For each product the name and address of each source from which your company obtained each PCB compound or mixture, and the amount of each PCB compound or mixture obtained from each source.

   d. The name and address of each of your company's facilities which handle such products (including production facilities and wholesale and retail outlets), and the amount of each product distributed through each facility.

   e. The name and address of each customer of each product, and the amount of each product obtained by each customer from each facility. For consumer products list only the total production of each product at each facility and the total number of customers. Do not provide the name and address of each customer of consumer products.

3. For each PCB compound or mixture used by your company in its operations other than for incorporation into its products, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. A description of each use.

   b. For each use the total amount of each PCB compound or mixture.

   c. For each use the name and address of each source from which your company obtained each PCB compound or mixture, and the amount of each PCB compound or mixture obtained from each source.

4. For each PCB compound or mixture reclaimed by your company, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. The total amount of each PCB compound or mixture reclaimed.

   b. The name and address of each source from which your company obtained PCB compounds or mixtures, and the amount of each PCB compound or mixture obtained from each source.

Figure 2. Questions sent by EPA to PCB users, concerning uses, importation, and reclaiming of PCB's.

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5. For each PCB compound or mixture disposed of by your company (with or without the involvement of other parties), for each company facility, during each year of 1971, 1972, 1973 1974, and the first two quarters of 1975:

   a. A description of each method of disposal.

   b. For each method of disposal the total amount of each PCB compound or mixture.

   c. For each method of disposal, the location of every disposal site, the name and address of each party involved in the disposal of each PCB compound or mixture, and the amount of each PCB compound or mixture disposed of by each party.

6. The composition of each PCB compound or mixture produced, imported, sold, reclaimed, used, and/or disposed of by your company since January 1, 1971.

7. The results of any and all sampling and analysis performed by your company, its agents or contractors since January 1, 1971, concerning the following:

   a. Concentrations of PCB compounds or mixtures in the effluent of any discharges by the company (into waters of the United States or Publicly Owned Treatment Works) or in the emissions of the company into the air.

   b. The flow and/or composition of any discharges or emissions by the company (into waters of the United States or Publicly Owned Treatment Works, or into the air) which contain PCB compounds or mixtures.

   c. Concentrations of PCB compounds or mixtures in receiving waters (both upstream and downstream) of any discharges by the company which contain PCB compounds or mixtures and concentrations of PCB compounds or mixtures in the air in the area of the company.

8. The methods by which PCB compounds or mixtures are transported to, by, and/or from your company, including:

   a. A description of each method of transportation, and the form in which PCB compounds or mixtures are transported by each method. Where different methods of transportation are used at different facilities specify which transportation method is used at each facility.

   b. The names and addresses of all known transporters of PCB compounds or mixtures.

9. All occasions (including spills) of which you are aware on which PCB compounds or mixtures have or may have been introduced into the environment. In particular, describe such occasions insofar as they involved PCB compounds or mixtures in their liquid state, as incorporated into closed systems, or as incorporated into open systems. For each occasion, indicate name and address of party involved; dates, time, and location of the discharge or spill; and the amounts involved.

10. A description of any adverse health or environmental effects which you know or believe to have resulted from the introduction of PCB compounds or mixtures into the environment. Indicate any specific occasions including dates, times, locations, amounts, and parties involved for which such effects are known.

11. Any and all other information which you possess concerning:

   a. The production, importation, reclamation, use, distribution, and disposal of PCB compounds or mixtures.

   b. The discharge of PCB compounds or mixtures into the environment.

In addition to the above, EPA would appreciate receiving any other information which you possess concerning the distribution and discharge of PCB compounds or mixtures by sources other than your company, including your company's customers and sources.

Figure 3. Questions sent by EPA to PCB users, concerning disposal, effluents, transportation, spills, hearth and environmental effects, and other data about PCB's.

MONS 063774

ANSI
C107.1-1974

American National Standard Guidelines for Handling and Disposal of Capacitor- and Transformer-Grade Askarels Containing Polychlorinated Biphenyls

Secretariat
National Electrical Manufacturers Association

Approved January 9, 1974
American National Standards Institute, Inc

Figure 4. Cover of industry standard for handling and disposal of PCB's.

MONS 063775

American National Standard

An American National Standard implies a consensus of those substantially concerned with its scope and provisions. An American National Standard is intended as a guide to aid the manufacturer, the consumer, and the general public. The existence of an American National Standard does not in any respect preclude anyone, whether he has approved the standard or not, from manufacturing, marketing, purchasing, or using products, processes, or procedures not conforming to the standard. American National Standards are subject to periodic review and users are cautioned to obtain the latest editions.

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Figure 4. (con.).

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Figure 5. Points covered in industry guideline for handling and disposal of PCB's.

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DISPOSAL METHODS

THERMAL INCINERATION FOR LIQUIDS

Incineration at 2200-2600°F with a retention time of 1-1.5 seconds. Venturi scrubber eliminates possibility air contamination. Cooling water is recycled and routinely checked for contamination. High aqeous waste are also incinerated by side injection into the system.

PHYSICAL CHEMICAL TREATMENT FOR HIGH AQUEOUS WASTE

Waste are pH controlled, settled, and filtered and passed through two carbon beds in series. Water passed through has invariably met at specs. No dctectable PCB's (less than 2 ppb).

SOLIDIFICATION

Solidification means solidifying liquids and sludges using a silicates-cement powder technique. After solidification, materials are disposed of in lined scientific landfill.

GELLATION

Liquids and sludges are polymerized or gelled in steel of fiber drumswhich are placed in a scientific landfill

SCIENTIFIC LANDFILL

Series of reinforced hypalon or reinforced chlorinated polyethylene lined cells in clay oil areas into which solid, sludges, stabilized chemicals, gelled liquids, solidfill liquids or sludges are disposited. A sump at the bottom of each cell recycles leachate to the physical-chemical treatment plant. A three-dimensional inventory is kept of waste in each cell. Surrounding ground and surface waters are routinely checked each month.

Figure 6. Methods developed by industry for disposal of PCB waste.

MONS 063778

AS A FUEL TO PRODUCE LOW ALKALI CEMENT POWDER

In Canada, there is being pioneered the concept of utilizing chlorinated chemical waste as a fuel and a supply of chlorine to produce low alkali cement powder. The waste material is fed into the fire box to supplement the fuel oil and burns at 2200 - 2600° f. The waste breaks down to water, carbon dioxide and hydrochloric acid. The acid neutralizes the potassium hydroxide present in the raw feed thus reducing the alkali in the cement powder. The cement kiln is perhaps the safest way to destroy PCBs. The temperature and retention time, approximately 16 - 18 seconds, are sufficient to reduce the PCBs.

This test program is currently under way at the St. Lawrence Cement Co. in Hamilton, Ontario, Canada.

Participants are: Ontario Water Resources Commission
St. Lawrence Cement Company
Chem-Trol Pollution Services, Inc.

Figure 7. Description of Canadian PCB study.

MONS 063779

federal register

THURSDAY, DECEMBER 27, 1973
WASHINGTON, D.C.

Volume 38 ■ Number 247

PART II

ENVIRONMENTAL PROTECTION AGENCY

■

WATER PROGRAMS

Proposed Toxic Pollutant Effluent Standards

No. 247—Pt. II——1

Figure 8. EPA proposed toxic pollutant effluent standards.

MONS 063780

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 129]

WATER PROGRAM

Proposed Toxic Pollutant Effluent Standards

Notice is hereby given that the Environmental Protection Agency, pursuant to the authority contained in section 307(a) of the Federal Water Pollution Control Act (the Act) as amended by the Federal Water Pollution Control Act Amendments of 1972 (33 U.S.C. 1251 et seq.) proposes a new Part 129, setting forth proposed effluent standards for toxic pollutants included in the list of toxic pollutants required by section 307(a)(1).

Section 307(a)(2) provides as follows:

Within one hundred and eighty days after the date of publication of any list, or revision thereof, containing toxic pollutant or combination of pollutants under paragraph (1) of this subsection, the Administrator, in accordance with Section 553 of title 5 of the United States Code, shall publish a proposed effluent standard (or a prohibition) for such pollutant or combination of pollutants which shall take into account the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms, and the nature and extent of the effect of the toxic pollutant on such organisms, and he shall publish a notice for a public hearing on such proposed standard to be held within thirty days. As soon as possible after such hearing, but not later than six months after the publication of the proposed effluent standard (or prohibition), unless the Administrator finds, on the record, that a modification of such proposed standard (or prohibition) is justified based upon a preponderance of evidence adduced at such hearings, such standard (or prohibition) shall be promulgated.

These proposed regulations establish effluent standards for the toxic pollutants listed below:

1. Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,8-endo - exo - 5,8-dimethanonaphthalene).

Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a - octahydro - 1,4-endo-exo-5,8-dimethanonaphthalene).

2. Benzidine and its salts (4,4'-diaminobiphenyl).

3. Cadmium and all cadmium compounds.

4. Cyanide and all cyanide compounds.

5. DDD (TDE) (1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane and some o,p'-isomers).

DDE (1,1-dichloro-2,2-bis(p - chlorophenyl)ethylene).

DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane and some o,p'-isomer).

6. Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro - 1,4-endo-endo-5,8-dimethanonaphthalene).

7. Mercury and all mercury compounds.

8. Polychlorinated biphenyls (PCB's) mixtures of chlorinated biphenyl compounds with various percentages of chlorination.

9. Toxaphene (chlorinated camphene).

The criteria and rationale employed to select these pollutants were summarised in the FEDERAL REGISTER Notice of September 7, 1973, vol. 38, No. 173, page 24343.

The following is a summary of the basis and purpose of the effluent standards proposed in this Part: The four basic factors considered in setting the standards were toxicological data, hydrodynamic data, sample margins of safety and calculations of the acute and chronic limitations for the standards. The primary basis for toxicological considerations came from the Water Quality Criteria which were proposed in October (38 FR 28646 et seq., Friday, October 26, 1973). These criteria were based in part on a report by the National Academy of Sciences and the National Academy of Engineering entitled "Water Quality Criteria", 1972 which is currently being published by the Environmental Protection Agency. The toxicity of the pollutants on the list, their persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms, and the nature and extent of the effect of the toxic pollutant on such organisms, were considered in the establishment of the Water Quality Criteria upon which these standards are based.

Water Quality Criteria published pursuant to section 304(a) of the Act are those concentrations which are acceptable in the receiving water body. The criteria were developed to protect a variety of water uses including industrial, agricultural, recreational, propagation of fish and wildlife, aesthetics and potable water supplies. The protection of fish and wildlife and potable water supplies was the most sensitive of the fresh water usages. In estuarine and marine waters, the protection of fish and wildlife generally yielded the more restrictive recommended limitations. The criteria, as proposed, were designed for both acute and chronic toxicological protection. Since protection against chronic effects requires more stringent criteria, the proposed Water Quality Criteria were devised from data or calculation designed to afford chronic protection.

Because proposed Water Quality Criteria utilize both acute and chronic toxicity data to derive a single acceptable ambient water concentration, it was necessary to utilize the data upon which the criteria were based to calculate proposed standards which provide for protection against both acute and chronic toxicological effects.

To avoid the effects of acute toxicity it was determined that organisms need not necessarily be protected at all times from concentrations exceeding the proposed Water Quality Criteria, since brief exposures to higher concentrations may be tolerated. It may be assumed that most mobile organisms will not remain in the immediate vicinity of the outfall for as long as the usual 96-hour test period. Thus, for protection in the immediate vicinity of the outfall, a concentration of one tenth the 96-hour LC_{50} was determined to provide an ample margin of safety (The 96-hour LC_{50} is that concentration derived from laboratory tests in which 50% of a group of test organisms survive after 96 hours of continuous exposure to a pollutant.) In order to achieve a concentration in the vicinity of the outfall which does not exceed the acute threshold, the discharger may either discharge the acute toxicity concentration and provide immediate diffusion through appropriate flow devices or reduce the concentration below the acute threshold.

To avoid the effects of chronic toxicity, an effluent standard is provided which is designed to ensure that, in most cases, the proposed Water Quality Criteria, which are intended to provide protection from chronic effects, are not exceeded over the long term in the receiving waters. This is achieved by limitation of the total weight of the pollutant which can be discharged into receiving waters of given size. To provide an additional margin of safety, the allowable weight discharged per unit of flow was reduced by safety factors designed to compensate, in part, for non-point sources of the pollutant, multiple discharges in a small area, industrial growth, and the difference in water storage times among lakes, estuaries, streams, and coastal waters. The standard for each type of receiving water is expressed as a number which, when multiplied by the rate of receiving water flow, yields the allowable weight of discharge of the pollutant per day from any facility.

These standards are not intended, however, to assure that Water Quality Criteria would be achieved in all receiving waters, since standards sufficiently restrictive to attain water quality criteria in (for example) small streams with extraordinarily large clusters of dischargers, would be overly restrictive for the usual case. These special "worst-case" situations are to be handled by the application of water quality standards through waste load allocations under section 303 of the Act. The resulting allocations may then be used to establish effluent limitations, if necessary, more stringent than the effluent standards set forth herein. Those limitations would then be incorporated into permits issued under section 402 of the Act.

Since there are no proposed Water Quality Criteria for benzidine, a different methodology was required for the derivation of an effluent standard. The methodology employed was designed to determine a level, of discharge which would result in an acceptable level of risk exposure to man, the primary affected organism. Effluent standards for benzidine were derived by the extrapolation of laboratory test animal data using conservative statistical methods, and are based upon a calculated level of risk of less than one case of tumor induction per million people exposed over an entire generation to drinking water from supplies derived from waters contaminated with the maximum permitted concentration of benzidine. It is recognized that certain inadequacies exist in the available data on which the benzidine standard is based. Therefore, it is reasonable to assume that these standards could be revised in the future. The Environmental

Figure 8. (con.).

MONS 063781

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.

POLYCHLORINATED BIPHENYLS

CRITERION:

.001 ug/l for freshwater and marine aquatic life and for consumers thereof.

Figure 9. Preliminary draft of EPA standard for water quality.

MONS 063782

DATE	CIRCUMSTANCES	CITY STATE	AMOUNT SPILLED	AMOUNT RECOVERED	METHOD OF DISPOSAL	COST	REPORTED TO EPA
6/ 8/71	Drums containing 5,500 lb started to leak en route	En route	Unknown	Unknown	None		No
10/11/71	Drum leaking en route, sent back	En route	Unknown	None	None		No
1/72	Rail car develops a leak	En route	Unknown	Unknown	Unknown		No
3/ 8/72	Truck accident, 5 transformers	Roanoke Rapids, NC	1000 gals Inerteen	Unknown	Unknown		No
5/ 8/72	Truck en route developed leak	Kingston, Tenn.	830 gal PCBs	11,500 drums of contaminated soil	55 gal sealed in concrete	$1.7 million	Yes
8/ 8/72	Truck accident	Havana, Ill.	400 gal	Unknown	Unknown		Yes
8/72	Transformer leak	Anderson, Ind.	15 gal	Unknown	Unknown		No
1/ 6/74	Transformer leak	Tuscaloosa, Ala.	80-100 gal	Unknown	Unknown		No
4/74	Transformer leak	Louisburg, Kansas	88 gal	Unknown	Unknown		No
5/20/74	Truck accident	Bedford, Ind.	Unknown	Unknown	Unknown		No
9/13/74	Transformer fell into Duamish River	Seattle, Wash.	783 gal	70-80 gal	Entombed in titan missle	$140,000	Yes
10/25/74	Transformer leak	Elizabeth, N.J.	10-100 lbs	Unknown	Unknown		No
Unknown	Transformer leak	Unknown	10-100 lbs	Unknown	Unknown		No
7/ 5/76	Transformer leak RR	Stanford, Conn.	10-100 lbs	Unknown	Unknown		No
9/10/76	Transformer leak RR	Bet. Phil. & Paoli, Pa.	10-100 lbs	Unknown	Unknown		No
11/10/76	Truck accident	Trion, Ga	130 gals	2,200 drums of contaminated soil	Entombed	$175,000	Yes
12/6/76	Truck accident	Erie, Pa	200 gals PCBs	Unknown	Unknown		No
12/27/76	Truck accident	Lawrence Al	650 gals PCBS	4,100 drums of contaminated soil	Entombed	$275,000	Yes
1/27/75	Truck accident	Rome, Ga	97 gals PCBs	193 drums of soil	Entombed	$5,000	Yes
8/9/75	Leaking drum on dock	Charlestown SC	60 gals PCBs	5 drums of soil	landfill	Unknown	Yes

Figure 10. The 20 identified spills that have involved PCB's.

MONS 063783

"OIL AND HAZARDOUS SUBSTANCE LIABILITY"

Sec. 311 of FWPCA, PL92-500, October 18, 1972

* 311(b)(2)(A) Designation of Hazardous Substances

Polychlorinated biphenyls PCB
Aroclor
Polychlorinated diphenyls

* 311(b)(2)(B)(i) Removability Determination

"...cannot actually be removed."

* 311(b)(2)(B)(ii-iv) Rates of Penalty for Non-Removable

PCB's Category A, Unit of Measurement lb - 1,$360/UM

311(b)(3) Non-Harmful Quantities

(being developed)

* 311(b)(4) Harmful Quantities

PCB's Category A, HQ in lb - 1

311(f)(2) Small Facilities Liability Limitations

(being developed)

311(j)(1)(A) Methods of Removal

(being developed)

311(j)(1)(c) Prevention

(being developed)

Figure 11. List of subjects covered in proposed EPA regulation under Section 311 of the Water Act.

MONS 063784

the 20 in which PCB's reached the water. This is the Duwamish River incident. The majority of the spills are transportation-related.

EPA is finalizing its proposed regulations under Section 311 of the Water Act, "Oil and Hazardous Substance Liability" (figure 11). At the present time, only four areas will be covered in the proposed regulation and the other four sections will be following next year, we hope.

MONS 063785

SOURCES OF POLYCHLORINATED BIPHENYLS IN WISCONSIN

Stanton J. Kleinert*

Abstract

The past and present users of PCB's are discussed and effluent sampling data are presented for municipal wastewater treatment plants and industries in Wisconsin. Data are also presented covering PCB levels in surface waters, fish, sediments, and snow melt. A general assessment of the PCB problem in Wisconsin is made with comments concerning the need for further study and regulation.

My report will summarize the work completed by the Wisconsin Department of Natural Resources and others to determine concentrations of PCB's in fish and to identify discharge sources in Wisconsin. Our interest in PCB's began in the late 1960's, when interfering substances were detected in the gas chromatograms of fish being tested for DDT. Later we were to learn these interfering substances were PCB's.

In 1970, the department collected fish samples along the Mississippi River bordering Wisconsin. Analysis revealed that fish from the Upper Mississippi River between Prescott and Pepin, Wisconsin, commonly exceeded the Food and Drug Administration tolerance level of 5 ppm (ref. 1). During 1971, Lake Michigan fish were collected and later tested in studies conducted by Dr. Veith in a University of Wisconsin study (ref. 2). Mean concentrations of PCB's expressed as Aroclor 1254 (wet weight) in the fish ranged from 2.7 ppm in smelt to 15 ppm in lake trout. Subsequent studies confirmed the presence of PCB's in fish in Lake Michigan and other waters of Wisconsin (ref. 3).

The search for PCB's in water was also underway at this time. Veith and Lee (ref. 4) sampled water from the Milwaukee River in 1969 and sampled effluents from selected municipal and industrial outfalls to the river in 1970. The analysis of water from the Milwaukee River indicated that PCB's were present in the river from West Bend to Lake Michigan and were being discharged through municipal and industrial effluents. In 1971, 11 municipal wastewater treatment plant effluents in Wisconsin were sampled by Dube, Veith, and Lee (ref. 5). Nine of the plant effluents contained PCB's identified as Aroclor 1254 and one contained Aroclor 1248. Studies of the Cedarburg wastewater treatment plant indicated that more than 70 percent of the PCB's coming into the plant were removed during the treatment process and comparatively high concentrations of PCB's were found in the digester and primary settling sludges.

The department surveyed many municipal wastewater treatment plant effluents in Wisconsin from 1972 through 1974. PCB's were detected in concentrations exceeding .05 ppb (the detection level for screening purposes) in more than half of the treatment plant effluents tested, even where there were no suspected industrial sources. In most cases, the discharge of PCB's was well below 1 ppb and .01 pounds per day. However, the higher concentrations of PCB's were found in sewage treatment plant effluents from industrial areas.

Tracing sources of PCB's reaching a large municipal wastewater treatment plant is a difficult and time-consuming task. The department is attempting to trace sources of PCB's reaching treatment systems where the final effluent exceeds 1 ppb. At the present time, we know of only two municipal wastewater treatment plants in Wisconsin which exceed 1 ppb—the Sheboygan and Portage facilities.

The main source of PCB's being discharged to the Portage treatment plant was found to be a facility that had used PCB's in the manufacture of carbonless copy papers prior to the summer of 1971. After ceasing the use of PCB's and after repeated cleanings of the holding tanks of the facility, the company substantially reduced the discharge. Residuals still remain, however, in the sewer system and the sewer sludges, resulting in an effluent of several ppb at the municipal sewage treatment plant. We are continuing to check sources of discharge to the Sheboygan treatment plant.

The department has checked effluents from iron and steel foundries and aluminum foundries. The testing has shown that the cooling water effluents from five to seven aluminum foundries contained PCB's ranging from 11.5 to 335 ppb. Close investigation revealed the common source to be leaking hydraulic fluids containing PCB's, which were used in die cast machines. We are working with company officials to correct the problem. PCB's have been found in the cooling water effluent of only one of nine iron and steel foundries checked to date and these were at a concentration of .9 ppb.

The Department of Natural Resources has tested the effluents of 17 pulp and paper mills for PCB's. The testing has revealed that nine of the mills that recycle waste-papers had measureable discharges ranging from .1 to

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MONS 063786

more than 25 ppb. Mill representatives indicate that the paper industry no longer uses PCB's and those found in wastepapers come primarily from carbonless copy papers that were produced prior to 1972. The old carbonless copy papers were widely used in forms and continue to enter the wastepaper market as old files are discarded. Aroclor 1242 is the principal form found in wastepaper, however, some Aroclor 1254 has also been reported. Because their solubility in water is low, we believe that most of the PCB's discharged from wastepaper mills are absorbed on fibers and other particulate matter. Mill wastewater treatment systems, which effectively remove particulate matter, should also remove PCB's.

The electrical industry continues to use PCB's as dielectric fluids in some capacitors and transformers. Although the units are sealed, some fluids may be lost as a result of accidents or disposal practices. In March 1975, the department corresponded with the major electrical companies in Wisconsin to determine current handling practices for capacitor and transformer fluids. The correspondence was followed by visits to many facilities. The companies contacted were aware of the PCB problem, but some were not aware of the recommended Guidelines of the American National Standards Institute (1974) for Handling and Disposal of Capacitor and Transformer Askarels (Fluids) Containing PCB's (ref. 6). We also found that some facilities were storing defective capacitors until a proper disposal method could be found. As a result of this survey, specific guidance was given to Wisconsin electric utilities for the proper handling and disposal of PCB's.

Snow samples were collected early in 1975 to determine if PCB's were deposited on land and water as fallout from the air. Analysis of the snow melt water from Racine, Kenosha, Madison, and Milwaukee revealed concentrations from .17 to .24 ppb. These values suggest that fallout of PCB's from the air may be a principal source of PCB's entering the waters of the State.

PCB's are present in sediments in harbors and streams near industrial areas. The sediments act as a reservoir where PCB's may be released slowly over a long period of time. Sediment samples have tested 3.5 ppm in the Milwaukee River near the Capital Drive Bridge, 9 ppm in Superior Harbor, and 72 ppm in the Fox River below the outfall of the Portage sewage treatment plant.

We have tried to work out a materials balance for PCB's entering the environment using the domestic sales figures provided by the Monsanto Company as well as other data. There are so many pieces missing from the puzzle, though, that our efforts to work out a materials balance have been unsuccessful. Some general comments can be made, however.

1. PCB's have been sold by the Monsanto Company for more than 45 years (ref. 7). The company has reported domestic sales of 795 million pounds of PCB's for the years 1957 through 1974. Aroclor 1242 accounted for 15 percent, Aroclor 1260 accounting for 11 percent, and Aroclor 1248 accounting for 7 percent of the sales. In 1974, the Monsanto Company's domestic sales of PCB's were reported to be 34 million pounds for use in closed electrical systems. In addition, the Office of Toxic Substances, EPA (ref. 8) has reported that foreign sales of PCB's in the United States in 1974 exceeded 375,000.

2. The PCB problem in Wisconsin is a fishery problem caused because residues have accumulated in certain fish in Green Bay and Lake Michigan and the Upper Mississippi River in excess of FDA tolerance level of 5 ppm. Laboratory experiments have shown that fish accumulate PCB's more than 100,000 times the levels present in the water (ref. 9). Therefore, PCB's in the water, even at ppt levels, have significance to the fishery resource.

3. Our data indicate that levels of PCB's in fish in the Upper Mississippi River have declined in recent years. We have not detected a corresponding decline in levels in Lake Michigan fish.

If Lake Michigan water contains an average of 10 ppt PCB's, then there are more than 100,000 pounds of PCB's in solution in the lake waters and there is probably a much larger poundage in the sediments. We have tested the major effluents of both municipalities and industries discharging to the Lake Michigan drainage in Wisconsin and estimate a discharge of about 2 pounds per day or 730 pounds of PCB's per year to Wisconsin's drainage to Lake Michigan. Most of PCB's identified in our testing of major effluents occur in the wastewaters of pulp and paper mills that recycle wastepapers.

Discharges of PCB's from pulp and paper mills that recycle wastepapers will diminish as the mills meet their discharge permit requirements. Wisconsin mills that recycle wastepapers are required to reduce their discharge of suspended solids from 131,000 pounds per day (for calendar year 1973) to 45,000 pounds per day by the 1977 compliance date. Recently one mill in the State, which uses only recycled papers, began operation of a new treatment system that has reduced the discharge of suspended solids from 40,000 pounds per day to 3,000 pounds per day. Tests at this facility revealed 39 ppb PCB entering the treatment system with only 1 ppb being discharged in the final effluent.

4. In our search for sources of PCB's entering the environment, we have not looked closely enough at fallout from the air. Our testing of snow melt suggests that fallout may be contributing much greater amounts of PCB's than are being contributed by industrial and municipal effluents. Trace concentrations in fallout over Lake Michigan and its watershed, which cover 67,900 square

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miles, could result in appreciable amounts of PCB's entering the waters of Lake Michigan.

Because PCB's are stable compounds with low vapor pressures, little loss is expected to occur through vaporization from disposal sites where capacitors and other equipment and materials have been disposed and covered with overburden. Entry into the air may be expected to occur at locations where papers are incinerated, at foundries where imported casting waxes containing PCB's are heated to high temperature, and at manufacturing facilities. PCB's adsorbed on fine particulate matter may also be entering the air, as windblown dust.

5. Further information is needed to define the amount of PCB's contributed to Lake Michigan and other waters through past accumulations in sediments. A University of Wisconsin study is currently underway in Southern Lake Michigan; this should provide some of the answers.

The Department of Natural Resources does not have the authority to regulate the sale or use of PCB's, but can adopt effluent standards. The department held hearings on two proposals for effluent limitations for PCB's on August 28-29, 1975. The first proposal would prohibit the discharge of PCB's and the second would limit the discharge to .005 mg/l or 5 ppb. The hearing record is being reviewed by the Natural Resources Board. No final decision has been made on an effluent standard as yet.

On September 10, 1975, Congressman Aspin of Wisconsin introduced a bill (HR 9525) to prohibit the introduction or delivery for introduction into commerce of PCB's. This bill is pending in the House Interstate and Foreign Commerce Committee, Subcommittee on Consumer Protection and Finance. This legislation would become effective 3 years after enactment providing industry with a 3-year changeover period to alternate substances.

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POLYCHLORINATED BIPHENYL USAGE AND SOURCES OF LOSS TO THE ENVIRONMENT IN MICHIGAN

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Abstract

Polychlorinated biphenyls (PCB's) are used in a wide variety of applications including dielectric fluids in transformers and capacitors; plasticizers in paints, inks, plastics, and coatings; hydraulic systems; heat transfer systems; investment casting waxes; and many more. This paper describes industrial uses of PCB's in Michigan and focuses on those uses which were found to be sources of environmental contamination. It describes PCB use figures supplied by several industries and concentrations detected in industrial and municipal effluents and sludges.

INTRODUCTION

Polychlorinated biphenyls (PCB's) are complex mixtures of chlorine-substituted biphenyl compounds and have been produced commercially in the United States since 1929. Their properties of nonflammability, stability, resistance to acids, alkalis, and other caustic chemicals, and low volatility under prolonged heating have made them useful in a wide range of industrial products.

Monsanto Chemical Company, the sole U.S. manufacturer of PCB's, recently released production and sales figures through 1974 (ref. 1). These showed that production and sales roughly doubled between 1960 and 1970, with nearly 80 million pounds sold annually in the United States by 1970.

Broadhurst (ref. 2) has summarized many of the uses of PCB's. The five largest uses for PCB's prior to 1970 were dielectric fluids in capacitors, plasticizer applications, transformer fluids, hydraulic fluids and lubricants, and heat transfer fluids. The list of other uses is lengthy.

Because of the widescale usage of PCB's, they have become distributed throughout the world. Since 1967, reports of PCB residues in fish, birds, water, sediments, and other environmental samples have been common. They are of concern in the environment because of their persistence, potential for biological magnification, and chronic toxicity.

By 1971, Monsanto recognized the environmental problems which had developed because of PCB's and initiated a program to phase out sales for all open-ended uses, finally limiting sales to uses in electrical capacitors and transformers. Many officials believed this action would result in rapid reductions in environmental contamination but little evidence of this has yet been documented.

Michigan officials have been studying the PCB situation since 1969 when excessive PCB residues were detected in Great Lakes fish. After development of adequate laboratory capabilities, we instituted a monitoring program for PCB's early in 1971 consisting of a statewide water sampling survey in inland waters and tributaries to the Great Lakes. Supplementary sampling has since been conducted on fish from inland and Great Lakes waters, stream sediments, potable water intakes, sanitary landfill runoff, municipal wastewater treatment plant effluents, and industrial discharges. Limited questionnaire surveys of industrial usage have also been conducted. This paper will report briefly on the industrial uses of PCB's that we have identified in Michigan and focus on those uses which were found to be sources of environmental contamination.

Electrical Applications

Prior to the 1971 Monsanto limitation of sales to the so-called "closed-system" uses, approximately 60 percent of U.S. sales were for electrical capacitor and transformer applications. In 1968, annual capacitor and transformer sales totaled approximately 30 and 16.8 million pounds, respectively (ref. 3).

While losses from the use of PCB's in these applications have been estimated as minimal (ref. 3), incorrect disposal practices and accidental losses from equipment and storage areas do occur and can result in environmental contamination.

In response to an industrial questionnaire sent to a cross section of Michigan industries in 1971, one major power company in Michigan reported an annual use of 562,000 pounds of PCB's (250,000 in precipitator transformers and 312,000 in capacitors). Company records showed annual losses of approximately 300 pounds of PCB liquids to soils from burst capacitors and 12,000 pounds from salvaged capacitors. This fluid from the capacitors was reportedly disposed of through waste

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haulers. Waste haulers then dispose of these wastes in many ways, including dust control on roads, sale of oils as fuel in low-temperature boilers, and treatment and discharge to municipal sewerage systems. Fluid recovered from precipitator transformers was returned to Monsanto for incineration. In the same industrial questionnaire survey, a smaller power company reported that it had been disposing of approximately 700 pounds of PCB's per year by mixing with other waste oils and using the oils for dust control on their driveway and parking lot.

In October 1975, a 55-gallon drum of PCB transformer oil on inventory at a Michigan power company developed a leak from a defective seam. Approximately 45 gallons of the fluid soaked into the ground, resulting in more than 100 cubic yards of contaminated soil having to be removed and disposed of in an approved landfill. This situation illustrates the lack of such proper safeguards as diking around storage areas and represents an example of environmental loss from a so-called "closed-system" use.

Most industries other than utility companies using electrical transformers containing PCB's contract either the transformer manufacturer or smaller companies for servicing and do not concern themselves with the problem of disposal of the waste fluids. Frequency of servicing appears to differ between industries, varying anywhere from every 6 months to 10 years.

While water sampling programs in Michigan have failed to identify any electrical applications of PCB's as major point sources of loss to aquatic situations, environmental losses do occur which have the potential of indirectly reaching watercourses through atmospheric fallout or leaching from contaminated soils at spill or disposal sites. Losses directly to water may occur on occasion but would be difficult to detect because of their intermittent nature.

Plasticizer Applications

Plasticizer applications represent the single largest "open-ended" or dissipative use of PCB's. PCB's are or have been used as plasticizers in most countries in a wide variety of consumer products, including paints, inks, copying paper, adhesives, sealants, plastic products, and textile coatings, many of which are traded internationally (ref. 4). Monsanto's U.S. sales figures for 1970 showed a volume of nearly 20 million pounds for plasticizer applications (ref. 1). Sales for this use were discontinued in 1971. Environmental losses from past sales will likely continue for a long period of time.

Papers used in the thermographic, xerographic, or pressure-sensitive copying processes have had PCB's added as plasticizers either in the ink or paper coatings. Recycling of these papers can result in contamination of food packaging materials and other paper products (ref. 3).

Effluents from paper recycling or deinking plants also become contaminated. In Michigan, paper industry effluents have been found to commonly contain from 1 to 10 μg/l of PCB's. Contamination of fish has been identified as high as 110 mg/kg in the Kalamazoo River downstream from Kalamazoo, Michigan, where Michigan's paper industry is primarily centered. Stream sediments in the Kalamazoo area contain as much as 360 mg/kg PCB's; this is believed to be a result of past deinking processes in the area. Lower level contamination continues from processing of recycled paper but most deinking mills have ceased operation over the past 10 years.

While Monsanto stopped sales of PCB's for paper applications in 1971, one Michigan paper company recently reported to the Michigan Department of Natural Resources that several raw products that they purchase still contain PCB's. Two coloring compounds reportedly have 23 and 500 mg/kg PCB's and nearly all of their wood pulp contains from 0.5 to 1.0 mg/kg.

Burning of waste papers containing PCB's, which occurs every day, undoubtedly results in atmospheric losses. PCB's have been detected in snowfall samples in Wisconsin (ref. 5).

The largest quantities of PCB's in plasticizer applications end up in dumps and landfills. Much of the material is in sealed containers or impregnated in plastics and is slowly released to the environment. Nisbet and Sarofim (ref. 6) reported that vaporization directly from paints, coatings, and plastics does occur, with losses as great as 20 percent. Open burning in landfills also releases PCB's to the atmosphere. Another source is loss to leachate from landfills. Samples of surface runoff water from nine landfills in Michigan showed five of the nine samples having PCB concentrations ranging from 0.04 to 0.30 μg/l, while the others contained less than 0.01 μg/l.

In 1970, the U.S. Food and Drug Administration identified milk contamination in Ohio, Georgia, and Florida resulting from use of a PCB-containing sealant in silos (ref. 3). In 1975 the Michigan Department of Agriculture investigated problems from this usage and found 76 dairy herds in Michigan with PCB's in milk ranging from a trace to 14 mg/l on a fat basis. Scrapings from silos on these farms contained PCB's up to 10,000 mg/kg. Eighty additional silos have been identified as having the PCB sealant and have been removed from use until a protective coating can be applied to eliminate transfer of PCB's to the cattle feed.

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Hydraulic Fluids

PCB's have found wide usage in hydraulic systems involving extreme pressure and high-temperature conditions. Annual U.S. domestic sales of PCB's for hydraulic uses totaled approximately 8 million pounds in 1970 (ref. 1). In Michigan, the automotive and metal finishing industries have used PCB-containing hydraulic fluids extensively. Industrial inspections and questionnaires documented past usage to have been as much as 878,000 pounds/year in individual plants, with most being collected and disposed of through waste haulers. Large losses of PCB's from these plants to municipal sewers or directly to surface waters have also been identified. Wastewater discharges from identified users of PCB-hydraulic fluids have had concentrations as high as 7.1 mg/l PCB's, indicating losses as great as 30 pounds per day. In a materials balance study, one industry which showed in its records that it was replacing approximately 30,000 pounds PCB's/year in hydraulic systems calculated that 10,000 pounds/year were entering the atmosphere through vaporization losses, 8,000 pounds/year in absorbents placed in landfills, 6,000 pounds/year lost to soils and drainage systems on plant property, 5,000 pounds/year going to waste haulers, with the remainder incinerated.

All industries that we have identified as using PCB's in hydraulic systems have converted to substitute products, mostly phosphate esters. Complete elimination of PCB residues from the systems has proved ineffective even with repeated flushings. Sampling of replacement fluids indicates PCB contamination as high as 100 mg/l. Residues in discharge lines combined with loss of contaminated replacement fluids appear to result in continued low-level discharges. Because of existing inventories and possible purchase from foreign sources or reprocessing companies, it is unlikely that all hydraulic systems not included in our surveys or questionnaires have been switched to replacement fluids. One facility which we investigated had an inventory of 9,000 gallons of PCB fluids in storage.

In summary, Michigan's surveys of hydraulic system usage of PCB's suggests that this has been a major source of environmental contamination and may continue to contribute to the problem to a lesser but still significant degree.

Heat Transfer Systems

PCB's heat transfer fluids have been used in place of steam or superheated water in many industries and large building complexes. They provide advantages of reduced explosion hazards, absence of corrosion problems, and have good heat transfer characteristics (ref. 4). In 1970, Monsanto sold approximately 4 million pounds of PCB's for this application but phased out all sales in 1972 (ref. 3).

From 1971 through 1973, Michigan identified at least 12 facilities discharging PCB's to surface waters or municipal sewers from this usage. Concentrations in some discharges were as high as 5.2 mg/l.

One automotive company in Michigan reported using 34,000 pounds of PCB's per year in heat transfer systems at three of its plants. The waste fluids were reportedly disposed of by industrial waste haulers. Another smaller plant reported loss of 800 pounds in 1972 and that approximately 700 pounds of this total was incinerated, 75 pounds disposed of in dumps, and 25 pounds lost to sewers and drains.

In another Michigan survey, a chemical company complex was found to have an effluent concentration of 35 µg/l resulting from heat transfer system losses. Heat transfer losses are not all from industrial facilities. Sampling of interceptor lines of the Detroit, Michigan, sewerage system resulted in the identification of heat transfer usage from two residential building complexes and one hospital as large sources of PCB input to the system.

Miscellaneous Uses

In 1971, Michigan officials found a PCB concentration of 6.6 µg/l in the waste lagoon of a soap and detergent company. The source was traced back to the company's usage of PCB's as a dedusting agent at 0.7 percent in one of its powdered products. The company had discontinued this usage in June 1970 and the PCB's were apparently leaching from contaminated lagoon sediments.

The investment casting wax industry has been recently identified as another user of PCB's (ref. 7). This casting method, which has largely replaced sand casting for production of low-tolerance-quality metal castings, uses formulated waxes as a basic molding mode. The waxes are injected into metallic dias to form the part shape and then coated with ceramic to form a final mold. The wax is removed by insertion of the mold in an autoclave, which melts the wax. Residues of wax are also secondarily removed by insertion of the molds in a furnace at 1,600° to 1,800° F. During these two procedures, the bulk of the wax is collected and usually recycled but a portion is lost to vaporization, cooling water contact, and poor housekeeping practices.

The waxes in use are obtained from a few major suppliers, one of whom is a major importer of decachlorobiphenyl from an Italian source. We have found twelve firms in Michigan using this casting process and several firms that reprocess their waxes. Our preliminary investigations indicate that most of the waxes contain approximately 20 percent of PCB's or polychlorinated terphen-

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yls (PCT's); one recent sample indicates the range may extend as high as 60 percent content in the wax. The nature of these casting operations, including both operational and storage modes, at many plants indicates strong potential for environmental loss. An effluent sample from one of the Michigan companies using investment casting wax contained 2.5 µg/l of PCB's.

During a telephone survey of 39 industries in Michigan during May 1975, several industries reported use of a toilet hand soap containing 0.05 percent PCB's by weight. Followup on these reports indicated that this product actually contains a chlorinated diphenyl oxide rather than PCB's.

Three industries in the telephone survey reported use of a hydrated lime product that contained about 0.5 mg/kg PCB's. This product was being used for water treatment and in production of glass pellets. No explanation was available on why the lime contained PCB's but it is assumed to be a contaminant rather than an additive.

Concentrations in Municipal Wastes

Because of the diversity of PCB usage, municipal wastewater is likely to receive PCB's from numerous domestic and industrial sources, many of which are listed above. Buckley (ref. 3) estimated that municipal outfalls would likely contribute less than 5 percent (300 tons) of total annual loadings (6,000 tons) to aquatic environments of the North American continent. His estimate was based on an assumed average PCB concentration of 10 µg/l in wastes serving a sewered population of 150 million people producing 130 gallons of sewage per person per day.

Sampling of 58 municipal wastewater treatment plant (WWTP) effluents throughout Michigan in 1973 showed an average concentration of 0.52 µg/l (table 1). This is considerably lower than Buckley's value of 10 µg/l used in his calculations but still exemplifies widespread contamination in municipal wastes, and documents that they are indeed a source of PCB loss to surface waters.

Much of the PCB's entering municipal waste treatment facilities are removed and become incorporated into the waste sludge. Table 2 shows PCB concentrations in the sludges from Michigan municipal plants sampled in 1973. Concentrations are much higher than in the effluents from the same plants. The average for all plants was 15.6 mg/kg, with individual values as high as 350 mg/kg. Disposal of these sludges may add to environmental PCB levels. Sewage sludges are commonly disposed of by incineration, spreading on agricultural land, or placing in landfills.

Discussion

While I have characterized in this report possible and proven sources of environment loss of PCB's in Michigan from several applications, I want to acknowledge that not all industrial effluents tested in Michigan contain measureable PCB levels. We have tested over 900 industrial samples, with approximately 40 percent of effluents sampled containing PCB's above our 0.1 µg/l laboratory sensitivity limit. Twenty-three percent of the industries tested had greater than 0.5 µg/l, 18 percent greater than 1 µg/l, 6 percent greater than 10 µg/l, and 2 percent greater than 100 µg/l. This represents a diversity of industries showing contamination and in many cases the source of effluent contamination could not be determined.

Since new industrial sources of loss are continuously being found, we feel we are far from eliminating the PCB inputs to surface waters by searching for point sources and taking corrective measures on a case-by-case basis. We are far from understanding the impact or comparative contribution of atmospheric losses but we feel these are probably very significant also.

In light of considerable environmental damage and economic impact of PCB contamination, an absence of any apparent decline in environmental concentration with current control methods, the ubiquitous nature of usage, the general lack of adequate disposal facilities, and the indication that atmospheric transport and deposition is also significant, the Michigan Department of Natural Resources urges that a national ban be pursued on all domestic and imported PCB's destined for use other than in transformers and capacitors, and that the critical or essential use of PCB's in transformers and capacitors be immediately and critically reviewed in light of current potential replacement products.

Feeling that existing legislation was inadequate to control PCB's, a group of Michigan legislators introduced a bill on August 14, 1975, to prohibit the manufacture, sale, and use of PCB's in Michigan for all applications other than for transformers and capacitors. The bill would provide for labeling, reporting, and disposal requirements and specifies penalties for violations. The bill calls for a stepwise elimination of PCB's with the sale, manufacture, and use of products containing 25 percent or more PCB's forbidden by January 1, 1976; 10 ppm or more forbidden after January 1, 1977; and 5 ppm or more forbidden after January 1, 1978. Public hearings on the bill are currently being conducted by the Michigan House Committee on Marine Affairs. [The bill was amended and voted out of committee on December 11, 1975. The amendment changed the maximum allowable concentration after January 1, 1977, to 1,000 ppm and 100 after January 1, 1978.]

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Table 1. Concentrations of PCB's in the final effluent from wastewater treatment plants throughout Michigan, Spring, 1973. Concentrations in micrograms per liter, dry weight.

City	Date	PCB's 1242	PCB's 1254	1242:1254
Adrian	3/7/73			0.26
Albion	2/22/73		0.34	
Ann Arbor	3/1/73		0.25	
Bay City	3/1/73	3.20		
Battle Creek	2/28/73		<0.10	
Benton Harbor-St. Joseph	2/28/73		0.20	
Brighton	3/1/73			0.33
Cadillac	3/28/73		0.53	
Charlotte	5/1/73		0.34	
Constantine	2/28/73		0.46	
Detroit	2/28/73	2.15		
Dexter	3/1/73		0.23	
East Lansing	5/2/73		0.18	
Escanaba	3/28/73			0.28
Essexville	3/1/73		0.10	
Flint	2/22/73		<0.10	
Gladstone	3/28/73		0.44	
Grand Haven	2/21/73		<0.10	
Grand Rapids	2/21/73		1.05	
Holland	2/21/73		<0.10	
Houghton-Hancock	3/27/73		0.18	
Iron Mountain-Kingsford	3/28/73		0.69	
Ironwood	3/27/73			0.29
Jackson	2/22/73		<0.1	
Kalamazoo	2/29/73			1.12
L'Anse	3/27/73			0.31
Lansing	4/18/73		0.22	
Manistique	3/28/73		0.63	
Marquette	3/27/73		0.29	
Marshall	2/22/73		0.15	
Menominee	2/28/73		0.57	
Midland	3/1/73		<0.10	
Milford	3/8/73			2.20
Monroe	5/4/73		<0.10	
Mt. Clemens	3/8/73			2.90
Mt. Pleasant	3/28/73		0.29	
Muskegon	2/28/73		0.88	
Muskegon Heights	2/28/73		0.18	
Niles	2/20/73		0.48	
Norway	3/28/73		<0.10	
Owosso	2/21/73		0.12	
Pontiac (Auburn)	3/12/73			0.60
Pontiac (E. Blvd.)	3/12/73			0.54
Port Huron	3/8/73			1.80
Saginaw	3/1/73			0.77
Sault Ste. Marie	3/28/73		0.73	
St. Ignace	3/28/73		0.31	
Three Rivers	2/21/73		<0.10	
Traverse City	3/7/73		<0.10	
Trenton	2/28/73		<0.10	
Warren	2/27/73		<0.10	
Wayne County	2/28/73		0.40	
Wyoming	2/21/73		0.22	
Ypsilanti	2/28/73			0.31
Ypsilanti Twp #1	3/1/73		<0.10	
Ypsilanti Twp #2	3/1/73		<0.10	

[a]Concentrations based on best fit of three standards: Aroclor 1242, Aroclor 1254, or a mixture of Aroclor 1242 and 1254 in a 1:1 ratio.

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Table 2. Concentrations of PCB's in the sludge from fifty-seven municipal wastewater treatment plants in Michigan, Spring 1973. Concentrations in milligrams per kilogram, dry weight.

City	Date	PCB's 1242	1254	1242:1254
Adrian	3/7/73			24.0
Albion	2/22/73		1.5	
Ann Arbor	3/1/73		1.1	
Bay City	3/1/73	352.0		
Battle Creek	2/28/73		2.8	
Benton Harbor-St. Joseph	2/28/73		13.8	
Brighton	3/1/73		<0.1	
Cadillac	3/28/73		<0.1	
Charlotte	5/1/73		6.8	
Constantine	2/28/73		2.1	
Detroit	2/28/73	32.1		
Dexter	3/1/73		3.2	
E. Lansing	5/2/73		4.6	
Escanaba	3/28/73		5.9	
Essexville	3/1/73		3.9	
Flint	2/22/73		6.3	
Gladstone	3/28/73		4.1	
Grand Haven	2/21/73		4.1	
Grand Rapids	2/21/73		11.8	
Holland	2/21/73		0.8	
Howell	4/26/73		15.0	
Houghton-Hancock	3/27/73		5.5	
Iron Mountain-Kingsford	3/28/73		9.5	
Ironwood	3/27/73		5.2	
Jackson	2/22/73		3.0	
Kalamazoo	2/29/73	23.3		
L'Anse	3/27/73		4.4	
Lansing	4/18/73		5.3	
Manistique	3/28/73		1.5	
Marquette	3/27/73		2.8	
Marshall	2/22/73		3.9	
Menominee	2/28/73		4.2	
Midland	3/1/73		2.9	
Milford	3/8/73			50.5
Monroe	5/4/73		3.3	
Mt. Clemens	3/8/73	175.0		
Mt. Pleasant	3/28/73		6.5	
Muskegon	2/28/73		12.7	
Muskegon Heights	2/28/73		11.0	
Niles	2/20/73		7.8	
Norway	3/28/73		<0.1	
Owosso	2/21/73		2.0	
Pontiac (Auburn)	3/12/73			12.1
Pontiac (E. Blvd.)	3/12/73			9.2
Port Huron	3/8/73			9.2
Saginaw	3/1/73		5.0	
Sault Ste. Marie	3/28/73		2.4	
St. Ignace	3/28/73		1.5	
Three Rivers	2/21/73		4.1	
Traverse City	3/7/73		1.8	
Trenton	3/28/73		<0.1	
Warren	2/27/73		<0.1	
Wayne County	2/28/73	2.0		
Wyoming	2/21/73		0.58	
Ypsilanti	2/28/73		2.0	
Ypsilanti Twp #1	3/1/73		<0.1	
Ypsilanti Twp #2	3/1/73		<0.1	

[a]Concentration based on best fit of three standards: Aroclor 1242, Aroclor 1254, or a mixture of Aroclor 1242 and 1254 in a 1:1 ratio.

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CHAIRMAN GARRETT: I applaud all the speakers for their interesting insights in these matters. At this point I'd like to call for questions from the floor.

MR. DON SKINNER (Environment Canada, Ottawa, Canada): I am from Canada, and I would like to address myself to Mr. Tom Kopp. Tests going on at St. Lawrence Cement in Ontario, to set the record straight, are being financed by the Government of Canada and the Government of Ontario. The participation in that program other than the suppliers of the waste is still up to EPA?

MR. THOMAS E. KOPP (Environmental Protection Agency, Washington, D.C.): Yes, sir.

MR. HOWARD A. FORMAN (United Electrical Workers, New York, New York): I would like to address my question to Mr. Kopp. You had mentioned how EPA is surveying the use and disposal of PCB's. I know that at least our use was not surveyed, we represent a very valuable source of information on PCB use, especially regarding capacitor plants and transformer plants. Does EPA plan to survey and try to get information from the various labor unions involved in the electrical manufacturing industry?

MR. KOPP: That is a very interesting idea, to survey the unions. I will discuss this with our Office of Enforcement. We'll get together and discuss it and if you'll let me have your name and address, we'll get back to you.

CHAIRMAN GARRETT: I have one question I'd like to ask Bob Durfee. There may be some question that may arise from this, but Bob, would you please describe the differences between the two terms mentioned just now, Aroclors and askarels.

DR. ROBERT L. DURFEE (Versar, Inc., Springfield, Virginia): Well, Aroclors are a trademark of Monsanto Company, and askarels are a class of fluids which by their nature do not form combustible products during an electrical breakdown in a dielectric system. There are several types of askarels; among them is the metalated PCB.

MR. RICHARD FERRY (Bio International, Inc., Woods Hole, Massachusetts): You told us about filtration of PCB's. Do you have a handle on the quantity of PCB's and how they are disposed of?

DR. DURFEE: The disposal of all solid wastes containing PCB's is by landfill. There is no incinerator operating at the present time that will accomodate solids and destroy the PCB. As far as the quantities are concerned, I really do not know what the total is going to be. If you say that all transformer fluids are cleaned up once every 5 years or something like that, then perhaps the quantity will be less than 1 percent, and this will be replaced by fresh PCB's.

MR. WILLIAM H. BUSCH (Illinois EPA, Springfield, Illinois): This is not so much a question as a concern. It seems like there is another open-ended source of PCB's in that most electrical capacitors, the small ones, end up as a throw-away item in home entertainment products.

Television sets, radios, and motor-starting capacitors ultimately fail and are discarded in landfills. It seems like we should be giving more attention to groundwater around landfills. This was touched on earlier today.

CHAIRMAN GARRETT: We have been considering this aspect.

MR. JACK MEDVILLE: Dr. Durfee described the control of U.S. manufacture of PCB's. Does the presentation indicate that the United States has shut off foreign manufacturers of PCB's?

MR. KOPP: We have no legal authority to control importation of PCB's into the United States.

MR. MEDVILLE: I will phrase the question differently. We have received here a number of figures of the amount that is going out and being reentered each year from U.S. manufacturing; is there an outlet on what is coming in from foreign nations?

MR. KOPP: The information we get is from the Bureau of Customs. That is maintained confidential, which is upon their request. Only bulk PCB's are reported. The amount of PCB's entering in equipment, such as transformers, we have no idea, but we are trying to identify the importers of capacitors and transformers to the United States.

MR. MARK WILSON: I am from Canada. I am not addressing my question to any particular member. Does anyone know if PCB's are still used in aircraft, and secondly, what will the offshore oil lines do? Are they bringing their own European hydraulic facilities in?

MR. KOPP: We have thought about this a great deal. We have also thought about ships that are coming into the United States from overseas, because of their hydraulic systems. We do not know of any PCB's being used in aircraft except in capacitors.

These things we are trying to get information on, and we hope to get more consultation with the members of the Organization of Economic Cooperation Development.

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