Photochemical Degradation of Chlorobiphenyls (PCBs)*

by O. Hutzinger and S. Safe† and V. Zitko**

Polychlorinated biphenyls (PCBs) are stable towards oxidation, hydrolysis and other chemical reactions which conceivably occur in the environment. Although there is little direct evidence available, it is generally assumed that PCBs, particularly those with a high chlorine content, are also quite resistant to metabolic change.

Over the past years photochemical degradation was shown to be a possible major route of environmental breakdown for a number of pesticides (1–4). Until relatively recently (5), however, simple chloroaromatic compounds have not received much attention. The limited interest of photochemists in compounds of this type can perhaps be explained by the commonly held view that there is generally little cleavage of the C–Cl bond in chloroaromatic compounds (6).

We have previously shown (7) that 2,2',4,4',6,6'-hexachlorobiphenyl, when irradiated at 3100 Å in hexane, photolyses rather readily to give products which are formed by loss of chlorine, rearrangement and condensation. We now wish to present a first report of our studies on the photochemical stability of a number of chlorobiphenyl isomers in hexane as well as on the breakdown of chlorobiphenyls under natural and simulated "natural conditions", with particular emphasis on polar products.

Considerable experience in laboratory irradiations of pesticides has accumulated (1, 3, 8) and an elaborate "weathering chamber", which also allows controlled irradiation, has been described (9). "Natural conditions", however, are difficult to simulate for water-insoluble compounds such as the PCBs Even in sunlight, irradiation experiments in solution are artificial since "unnatural" organic solvents have to be used Irradiations of chlorobiphenyls in thin films, in the gas phase (both in the presence of water or water vapor) or in aqueous suspension are likely to be closer to the natural environmental conditions to which PCBs are actually exposed.

Equipment and Methods

Gas chromatographic (glc) separations were carried out with a Hewlett Packard model 5750 chromatograph using a flame ionization detector and an 8 ft × ¼ in stainless steel column containing 3% SE-30 on acid washed Chromosorb W (60/80 mesh). Temperature was isothermal or programmed as indicated. Quantitative data were obtained with a Packard A7901 gas chromatograph equipped with a 6 ft × ½ in 4% SE-30 column and an electron capture detector using the conditions previously described (10)

Combined glc mass spectral data were recorded with a Hewlett Packard model 5750 instrument, using a 6 ft × ¼ in glass column, coupled to a DuPont/CEC 21-491 mass spectrometer via a single stage jet separator

A DuPont/CEC 21-110B mass spectrometer equipped with a direct introduction-constant temperature probe (11) was used for obtaining spectra of individual samples

The infrared (ir) spectra (thin films) were recorded on a Perkin Elmer 237 spectrophotometer

Thin-layer chromatography (tlc) was carried out on precoated Merck silica thin layer plates (F-254) and plates (100×20 cm) coated with

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Merck silica gel (F-254, 0.9 mm thickness). Solvents used were hexane and (A) 1,1,1-trichloroethane–hexane (5:1), (B) hexane–acetone (3:1), (C) benzene–ethyl acetate (12:1), (D) benzene–chloroform (2:3). The chlorobiphenyls were synthesized as described before (12,13). Aroclor 1254 was a gift of Monsanto Co.

Sources of ultraviolet light for the irradiation experiments were as follows:

(i) Sun: direct sunlight at Halifax, N.S. during the period July to September 1971.

(ii) Photochemical reactor: Rayonet (the Southern N.E. Ultraviolet Co.) using 16 R.P.R. 3100 lamps (3100 Å). The temperature was maintained at 14±2°.

(iii) Blacklight: four General Electric F40BL fluorescent lamps mounted with reflective backing ca. 15 cm above the samples. The temperature at this distance was 30–33°.

(iv) Sunlamp: General Electric 275 W "Sunlamp", one per dish at ca. 25 cm distance (temp. 35–40°). For irradiation of chlorobiphenyl–water vapor, four lamps per 500 ml quartz tube were mounted horizontally at ca. 10 cm. distance.

Experiments and Results

Stabilities of Chlorobiphenyls at 3100 Å in Hexane Solution

Time study of 2,2',5,5'-tetrachlorobiphenyl decomposition—2,2',5,5'-Tetrachlorobiphenyl (50 mg) in hexane (300 ml) was irradiated in the Rayonet reactor with N_2 bubbling through the solution. 50 ml Aliquots were removed from the reaction vessel at 2, 4.5, 17, 41 and 89 h. Good quantitative data could not be obtained for the 89 h sample, probably because much of the material had polymerized. Chromatograms observed after injecting equal amounts of these aliquots and using a flame ionisation (F.I.) detector are shown in Fig. 1. Percentages of starting material remaining after different irradiation times are also presented in Fig. 1. These data were obtained by measuring the area under the peak with retention time identical to the starting material

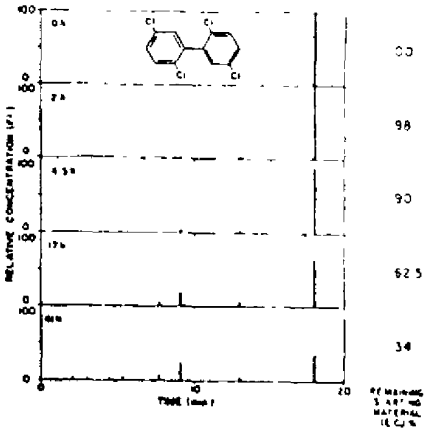

FIGURE 1 Irradiation of 2,2',5,5'-tetrachlorobiphenyl for different times, chromatograms and percent starting material remaining.

using an electron capture (E.C.) detector. Mass spectral and glc data for the 41 h sample are given in Fig. 2.

Comparative stability of chlorobiphenyl isomers—A 0.1% solution (3 ml) of the chlorobiphenyl hexane was flushed for 3 min with nitrogen, stoppered and irradiated in the Rayonet reactor for 24 h. The volume of the solution was removed from the quartz reaction cell and, after rinsing with hexane and evaporation of some of the solvent, adjusted to 3 ml. Equal amounts of the irradiated solution and the original solution

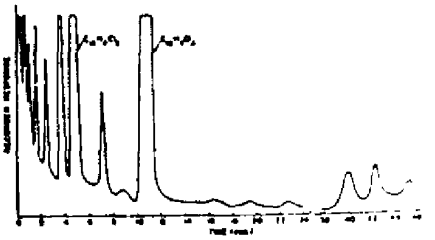

FIGURE 2 Chromatogram and mass spectral data for the 41 h sample. Oven temperature 150° isothermal at 20 min beginning of programming (4°/min). A number of further peaks were observed after 46 min.

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Table 1. Relative Photochemical Labilities of some Chlorobiphenyl Isomers

Compound	Starting material remaining after 24 h at 3100 Å in Hexane
Tetrachlorobiphenyls	%
3,3',4,4'-	32
2,2',6,6'	29
2,2',5,5'-	33
2,2',4,4',5,5'-Hexachlorobiphenyl	3 S
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	<1

were injected into the gas chromatograph, and the areas under the peak corresponding to the starting material compared (Table 1) No immediate correlation can be seen between steric hindrance of o-chlorine substitution or uv spectra (14) and photochemical lability, although chlorobiphenyls with high chlorine content seem to degrade more rapidly.

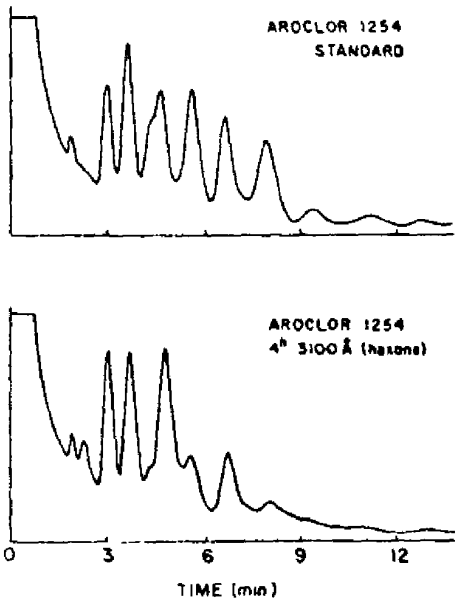
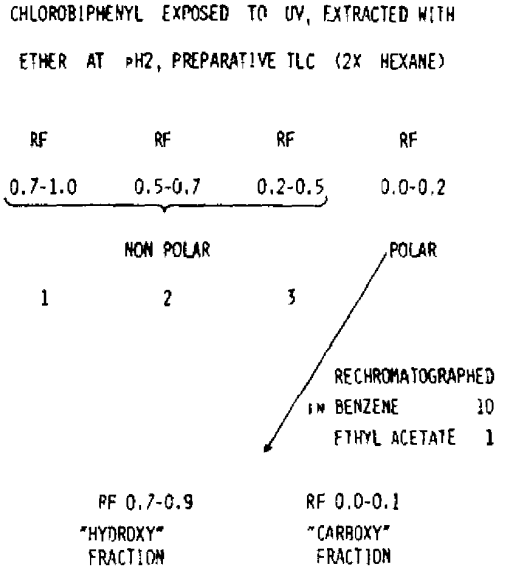


Figure 3 Chromatogram of Aroclor 1254 before and after irradiation Glc conditions of (10)

Stability of Aroclor 1254—Aroclor 1254 (20 mg) in hexane (3 ml) was irradiated for 4 h at 3100 Å in the presence of air Examination of the irradiated mixture and standard Aroclor 1254 by glc shows gross differences with tendencies toward shorter retention times (Fig 3)

Irradiations in Sunlight; Under Simulated "Natural" Conditions and in Solvent Mixtures Containing Water

Aroclor 1254 I; Aqueous dioxane suspension at pH 9—A suspension of Aroclor 1254 (2 g) in a mixture of dioxane (150 ml) and water (350 ml) containing sodium bicarbonate (0 5 g) was irradiated in the Rayonet reactor for 24 h with air bubbling through the mixture After this period another portion of sodium bicarbonate (0 5 g) was added, and the irradiation continued further for 24 h The mixture was worked up as shown in Scheme 1 Preliminary mass spectral data for the crude nonpolar fractions one, two and three indicated the presence of only chlorobiphenyls since no ions containing oxygen corresponding to hydroxychlorobiphenyls or chlorodibenzofurans were detected. The mass spectrum of the crude



Scheme I Separation-scheme for irradiated chlorobiphenyls

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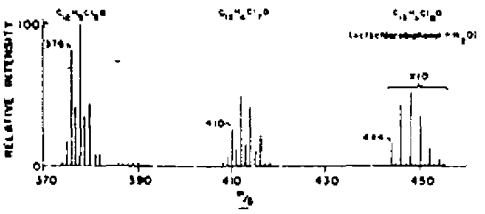

FIGURE 4. Partial mass spectrum (70 eV, probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment I. The chlorine isotope pattern for the Cl_4 and Cl_5 compounds are distorted due to impurities or fragment ions.

"hydroxy" fraction, part of which is shown in Fig. 4, indicated the presence of compounds formed by the addition of water to chlorobiphenyls. Hydroxy and carbonyl stretching frequencies in the infrared spectrum of the crude "carboxy" fraction (Fig. 5) are indicative of the type of compounds present in this mixture.

Aroclor 1254 II; Irradiation as thin film—Aroclor 1254 (0.5 g) was dissolved in benzene (3 ml), and this solution spread over a circular pyrex dish (diameter, 35 cm). The benzene was allowed to evaporate slowly in a way to ensure formation of a uniform Aroclor 1254 film. Water (3 ml) was added, and the dish was covered with plastic film. Water was frequently replaced during the Blacklight one-week irradiation. The irradiated product was fractionated according to Scheme 1. Preliminary mass spectra of the crude nonpolar fractions 1 and 2 (in this experiment no material

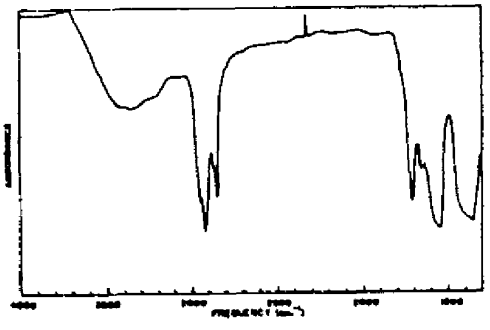

FIGURE 5. Partial infrared spectrum (thin film) of "carboxy" fraction from Aroclor 1254 irradiation experiment I.

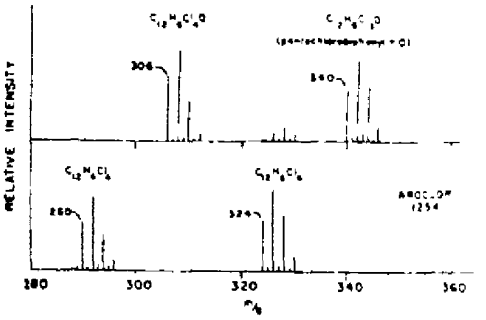

FIGURE 6. Partial mass spectra (70 eV, probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment II (top)) and standard Aroclor 1254 (bottom, ions <340 not shown).

corresponding to 3 was detected) showed only the presence of chlorobiphenyls. A mass spectrum of the crude "hydroxy" fraction (Fig. 6) showed ions which can be most easily explained as resulting from hydroxychlorobiphenyls. The ir spectrum of the crude "carboxy" fraction was almost identical to that from experiment I (Fig. 5).

Irradiations of 2,2',5,5'-tetrachlorobiphenyl—Some information on the types of products formed from 2,2',5,5'-tetrachlorobiphenyl on irradiation under a variety of conditions is given in Table 2. Samples were fractionated as

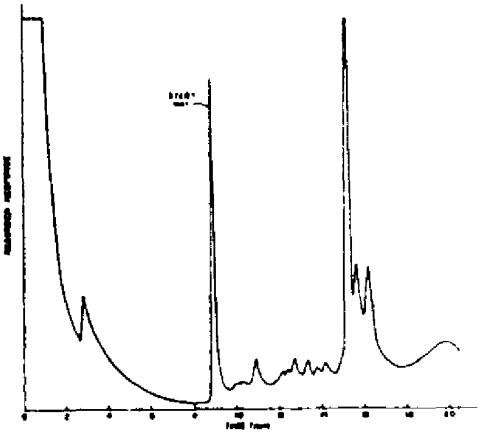

FIGURE 7. Chromatogram for 2,2',5,5'-tetrachlorobiphenyl irradiation experiment II. Oven temperature programmed from 150° at 10°/min until 310. A number of further peaks were observed after 20 min.

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Table 2. Photochemical Decomposition of 2,2',5,5'-Tetrachlorobiphenyl.

Experiment number	Irradiation conditions	UV source	Time	Types of products formed[a,b]			
				"Polar" products		"Nonpolar" products	
						Retention time[c]	
				"Hydroxy-"	"Carboxy-"	Short	Long
1	Aqueous suspension (+ emulsifier)	sun	2 mo	−	+	(+)	+
2	Thin film	sun	2 mo	(+)	+	(+)[d]	+[d]
3	Thin film	sun lamp	24 h	(+)	+	(+)	+
4	Thin film	black light	1 wk	(+)	+	(+)	+
5	Dioxan-2N NaOH solution	reactor	16 h	−	+	+	+
6	Aqueous dioxane solution + $FeCl_3$	reactor	16 h	(+)	+	+	+
7	Vapor (refluxing with water)	sun lamp	16 h	−	+	(+)	+

[a] + = present, (+) = present in small quantities; − = not detected.
[b] For further description of products, etc. see text.
[c] Glc retention time shorter or longer than starting material (2,2',5,5'-tetrachlorobiphenyl).
[d] See Fig. 7.

described in Scheme 1. The nonpolar fraction was analyzed by glc (e.g. Fig. 7).

"Carboxy"-type compounds were indicated in all experiments by the chromatographic properties of a portion of the reaction products which were similar to the corresponding fractions from the Aroclor 1254 irradiation experiments I and II (i.e., $R_f < 0.1$ in solvents A–C; high R_f in aqueous methanol mixtures).

The presence of "hydroxy"-type compounds was indicated by:

(i) chromatographic comparison of the appropriate fractions with authentic hydroxy- and dihydroxybiphenyls in solvent systems A, (R_f 0.3–0.8); B, (R_f 0.3–0.7) and C, (R_f 0.4–0.8), and

(ii) by reacting the "polar" fractions with dansyl chloride (1-dimethylaminonaphthalene-5-sulfonyl chloride) and comparing the chromatographic properties (solvent D; R_f ca. 0.75 for monohydroxy and ca. 0.4 for dihydroxy compounds) and in situ fluorescence excitation (350 nm) and emission (525 nm) wavelength with those of dansyl derivatives of authentic hydroxy and dihydroxybiphenyls (see reference 15 for the general method).

Discussion

The photolysis of chlorobiphenyls reveals a number of degradative reactions which occur on irradiation in sunlight and a number of laboratory conditions. In hexane, the most prominent reaction was the progressive reductive dechlorination of these compounds as well as formation of polymeric materials. Irradiation of Aroclor 1254 in hydroxylic solvents at pH 9 yields compounds corresponding to the addition of water to the PCB molecules and a more polar carboxylic acid fraction. The same sample irradiated as a thin film does not yield the water-addition products, but mass spectrometry reveals the presence of new hydroxylated species. This experiment also gives a more polar "carboxylic" fraction. Data for a number of different irradiations of 2,2',5,5'-tetrachlorobiphenyl indicate that dechlorination, formation of polymers, and carboxylic products as well as hydroxylation, does occur.

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The present photolytic work thus reveals decomposition of PCBs by both oxidative and reductive pathways

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Rates and Routes of Transport of PCBs in the Environment

by Ian C. T. Nisbet* and Adel F. Sarofim†

Polychlorinated biphenyls (PCBs) are one member of a class of chlorinated organic compounds which give rise to concern, because of their wide dispersal and persistence in the environment and tendency to accumulate in food chains, with possible adverse effects on animals at the top of the food webs, including man. In the past, attention has been concentrated on chlorinated hydrocarbon pesticides, such as DDT, dieldrin, heptachlor and HCH (hexachlorocyclohexane). More recently attention has been focused on PCBs and on chlorinated dibenzodioxins. Likely candidates for future attention are hexachlorobenzene, chlorinated dibenzofurans, and chlorinated phenols. In the past, such compounds have generally been studied individually. As the number of compounds giving rise to concern increases, there is an urgent need to establish uniform monitoring schemes and generalized models describing environmental transport and bioaccumulation which will be applicable to all compounds with these properties. Models such as the global monitoring scheme outlined by the SCEP study (1), and the global transport model outlined recently by Woodwell et al. (2), are needed in order to help identify sources of environmental contamination, to establish acceptable levels of discharge, and to estimate the effectiveness of different control strategies.

This paper summarizes the fragmentary knowledge available about production, uses, and losses of PCBs, and attempts to define the major routes of transport and reservoirs of PCBs in the environment. It discusses only production and uses within North America, and distribution of PCB residues in North America and adjacent seas (the eastern half of the North Pacific Ocean and the western half of the North Atlantic). It is expected that the picture will be generally similar for other areas where PCBs have been used extensively (i.e., industrialized regions, primarily in the North Temperate Zone), with minor differences depending on local patterns of use and disposal. However, references to studies made in Europe and Japan are made in this paper where they help to fill gaps in the North American picture.

Although we attempt to cover all the important environmental aspects of the use and distribution of PCBs, much of the discussion in this paper is extremely speculative. One of its main purposes is to point out the most important gaps in knowledge which must be filled before firm estimates can be made of present and future levels in the environment.

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Production and Use in North America

The sole manufacturer of PCBs in North America is the Monsanto Company. Commercial mixtures are sold under the trade name Aroclor and are distinguished by numbers, in which the first two digits 12 specify polychlorinated biphenyls and the last two digits the approximate percentage of chlorine in the mixture (3). In November, 1971, Monsanto released figures for U.S. domestic sales of Aroclors during the period 1963–70, summarized here in Figs. 1 and 2, where they are divided according to category of use and grade of Aroclor.

Prior to Monsanto's voluntary reduction of sales in September, 1970, approximately 60% of

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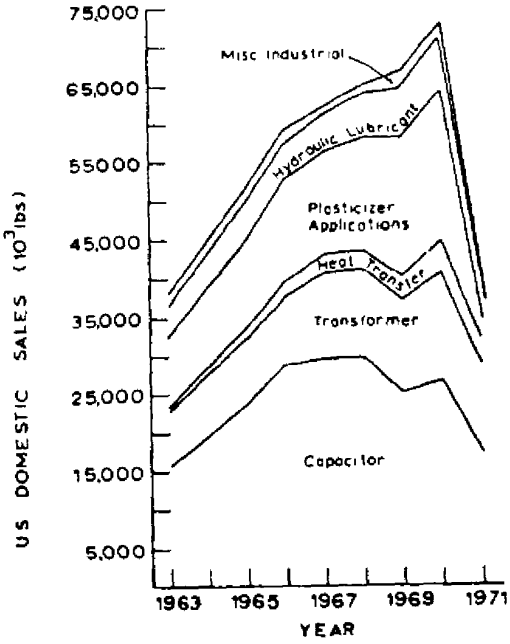

FIGURE 1 U S domestic sales of PCBs by category

sales were for closed-system electrical and heat transfer uses, 25% for plasticizer applications, 10% for hydraulic fluids and lubricants, and less than 5% for miscellaneous applications such as surface coatings, adhesives, printing inks, and pesticide extenders. Exports by Monsanto have averaged 13% of domestic sales over the period 1963 to 1970 Imports are thought to be small, comprised primarily of plasticizers in resins and adhesives, transformer oils and capacitor fluid in electrical equipment. Exports to Canada should be of the order of 7% of U S. sales and are included in this model of North America.

Monsanto has restricted sales of Aroclors based on consideration of either the possibility of contamination of food products or its inability to control or monitor possible losses into the environment. The fraction of sales for use in confined systems, primarily electrical applications, will increase to approximately 90 percent in 1971 and to 100% in 1972 The higher chlorinated Aroclors, 1254 and above, comprised approximately 30% of sales prior to 1971 Their share of the reduced sales in 1971 is expected to fall to 22% Aroclor 1242 is being replaced with Aroclor 1016 having a similar composition but with isomers containing 5 or more chlorine atoms removed

The breakdown by grade of the current uses of PCB is: electrical capacitors, mainly Aroclor 1016 with limited usage of Aroclor 1221 and Aroclor 1254; electrical transformers, Aroclors 1242, 1254 and 1260; vacuum pumps, Aroclor 1248 and 1254, and gas transmission turbines, Aroclor 1221 and 1242. The breakdown by PCB grade of former uses include Aroclors 1232, 1242, 1248, 1254, and 1260 for hydraulic fluids; Aroclor 1242 for heat transfer systems; Aroclors 1248, 1254, 1260, 1262, and 1268 for plasticizers in synthetic resins, Aroclors 1221, 1232, 1242, 1248 and 1254 for adhesives, Aroclors 1221, 1232, 1242, 1248, 1254 and 1268 for plasticizers in rubbers, Aroclors 1242, 1254 and 1268 for wax extenders; Aroclors 1254 and 1260 for dedusting agents; Aroclor 1254 for pesticide extenders, inks, lubricants, and cutting oils; and Aroclor 1242 for carbonless reproducing paper.

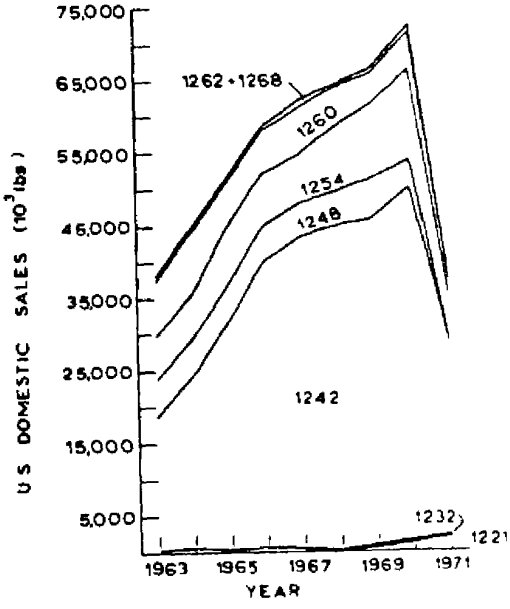

FIGURE 2 U.S domestic sales by PCB grade

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Data on production outside the U S are not available It has been estimated (4) that the Japanese production is 26 million pounds per year, 40–50% for capacitors, 15% for transformer oil, 10–15% for heat transfer fluid, 5% for plasticizers, 15% for carbonless duplicating paper, and 5—10% for export

Routes into the Environment

As in the case of most industrial chemicals, loss figures for PCBs are practically non-existent. Possible routes into the environment include (1) leaks from sealed transformers and heat exchangers; (2) leaks of PCB-containing fluids from hydraulic systems which are only partially sealed, (3) spills and losses in the manufacturing either of PCBs or PCB-containing fluids; (4) vaporization or leaching from PCB-containing formulations; (5) disposal of waste PCBs or PCB-containing fluids.

Examples of losses by each of these proposed routes include leaks from faulty heat exchangers in the contaminated Japanese rice oil (5) and contaminated chicken feed (Holly Farms) incidents; leakage of hydraulic fluid from an air compressor in Escambia Bay, Florida (6); the indirect evidence of possible losses during manufacture provided by the high level of PCBs in catfish in waters near Anniston, one of the two sites at which PCBs are manufactured in the U.S. (7); the leaching of PCBs from silos by sileage (7) and the use of waste electrical insulator containing PCBs as solvent in herbicide treatment of power rights-of-way near Martinsburgh, West Virginia (7). Other unreported disposal of scrap undoubtedly occurs into sewers (8). Statistical information on such losses is not available but could be generated by an accounting of PCB inventories and disposal by major users. To meet the problem of scrap disposal, Monsanto has set up a disposal system with a capacity of 10 million pounds per year for their customers. Within a year of announcement of the service, 500,000 pounds of waste PCBs had accumulated at the disposal site, where it was held in storage, pending the completion of an incinerator (9).

Another waste disposal problem is that of PCB-containing products including the PCB-impregnated paper in capacitors, caulking compounds, and carbonless duplicating paper. It has been postulated that the PCBs may be vaporized during incineration Based on studies into the incineration of PCBs and pesticide residues, municipal incinerators meeting design guidelines of a residence time of 2 seconds at 2000°F are expected not to be a significant source of PCBs (9, 10) Poorly operated commercial and municipal incinerators, small domestic and apartment incinerators, and open-burning dumps may, however, be major sources of emission, but data are not presently available Another problem is that of leaching from dumps Again, data are scarce, but analysis (11) of stagnant water close to a sanitary landfill indicated levels below the detection limit of 4 ppb

Quantitative Estimates of Rates of Loss into the Environment

It is unlikely that reliable quantitative estimates of past losses of PCBs into the environment will ever become available However, in order to assess the biological significance of the PCBs now in the environment, it is necessary to make some numerical estimates, however rough The following calculations are intended to provide order-of-magnitude estimates of rates of loss Figure 3 shows qualitatively some of the many possible routes of loss into the environment

Estimates of the rates of loss and disposal of Aroclors in 1970 will be based on rough guesses of the useful service life in different applications Transformers are fairly permanent installations, and it is therefore estimated that only 10% of sales of transformer fluid is to replace oil that was scrapped and that the remaining 90% is for new units. The useful life of capacitors, especially those used in small items such as fluorescent light ballasts, is expected to be under a decade, and it is therefore estimated that the rate at which the capacitors are discarded, primarily into landfill dumps, is equal to half the rate of production (Figure 1 indicates a doubling period for sales of about 10 years) A similar figure is assumed for the scrapping of heat exchangers, but it is expected that the replacement of fluid decomposed under extreme thermal conditions would have led, in the past, to additional direct losses, primarily into sewers It is estimated that the rate of vaporization of plasticizer amounts to 10 to 20% of

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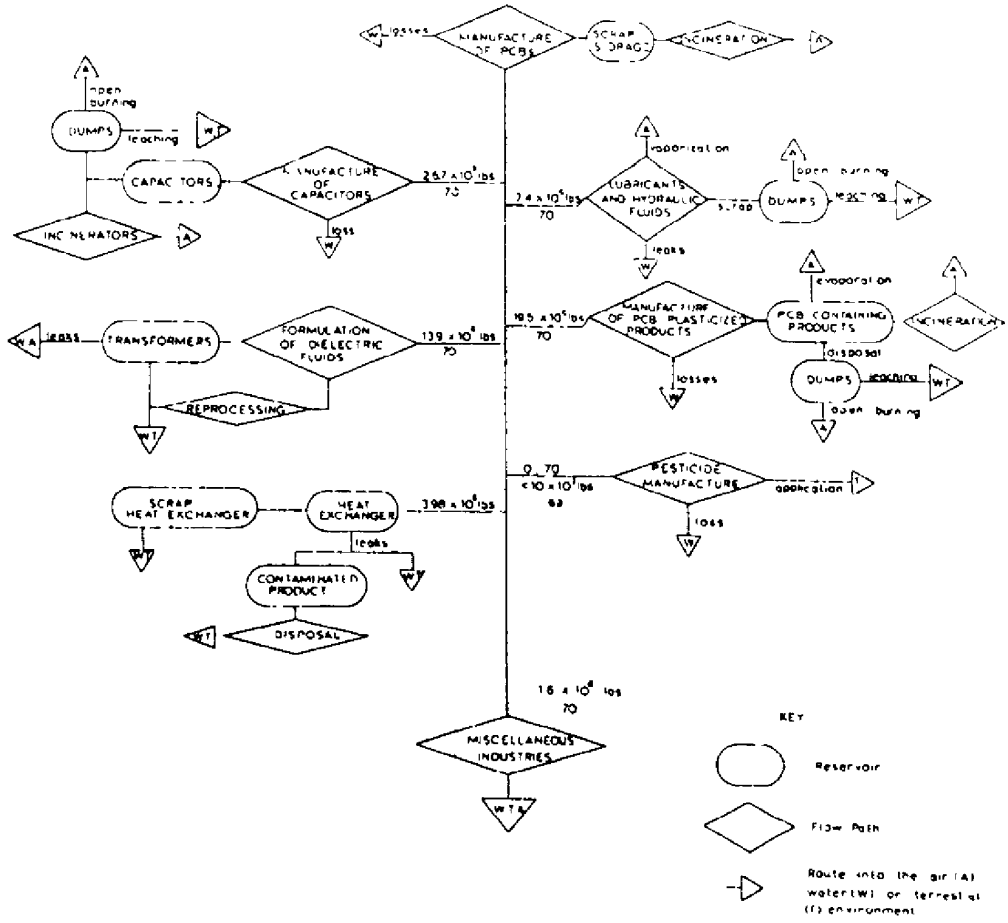

FIGURE 3 Possible routes of PCBs into the environment

sales (12) Since many plastic objects have relatively short useful lives the rate of disposal of plasticizers into dumps is assumed to equal the residual 80 to 90% of sales. Hydraulic fluids and lubricants are rately re-used, and it is therefore assumed that a major fraction of these fluids used for this purpose, together with those going into the miscellaneous applications, were scrapped at rates approximately equal to those of corresponding sales

On the basis of these gross estimates, it appears that only about 20% of the 1970 sales in North America, some 7×10^3 tons, represented a net increase in the amount of PCBs in service, in transformers, heat exchangers and capacitors The remainder is assumed to have been discharged into the environment, $1\text{–}2\times10^3$ tons by evaporation of plasticizers, $4\text{–}5\times10^3$ tons by leaks and disposal of hydraulic fluid and lubricant plus small amounts by disposal of heat transfer and tra-

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Table 1 Gross Estimates of Rates of Input and Accumulation of PCBs in North America in 1970.

Category of input	Rates (tons/year)	PCB Grade
Vaporization of plasticizers	$1-2\times10^4$	Mainly 1248 to 1260
Vaporization during open-burning	4×10^3	Mainly 1242
Leaks and disposal of industrial fluids	$4-5\times10^3$	1242 to 1260
Destroyed by incineration and open burning	3×10^3	Mainly 1242
Disposal in dumps and landfills	1.8×10^4	1242-1260
Accumulation in service	7×10^3	1242-1254

Reservoir	Accumulation (tons)	
	PCBs	ΣDDT
Soil (excluding dumps)	1.5×10^4	3×10^4
Oceans (adjacent to North America)	1.5×10^4	10^4
Fresh water (dissolved or in suspension)	10^3	$\sim10^2$
Fresh water sediment	2×10^4	?
Biota	$<10^3$	$<10^3$

former oils, and 22×10^3 tons by disposal in incinerators, dumps and sanitary landfills. Of the latter, we estimate (13) that 10 to 20% (3×10^3 tons) were destroyed by burning, and 2% (4×10^3 tons) were vaporized, mainly by open burning of wire scrap, auto components, and material in dumps.

Routes into the Environment

The total rate of loss of PCBs is thus estimated to have been of the order of 1.5 to 2×10^3 tons/year into the atmosphere, 4 to 5×10^3 tons/year into fresh and coastal waters, and 1.8×10^4 tons/year into dumps and landfills. The input into soils via the use of Aroclors as pesticide extenders is believed to have been small, less than 10 tons/year, on the basis of reports of purchases for this purpose. The unauthorized and unrecorded use of scrap PCBs as pesticide extenders is difficult to estimate but has probably been small. Direct discharge into the oceans, e.g. by dumping of hydraulic fluids and lubricants from ships, has probably been of relatively small magnitude, but may have been locally significant (49).

Most of the PCBs discharged into the atmosphere will have been Aroclor 1248 to 1260 vaporized from plastic resins, augmented primarily by 1242 vaporized from burning dumps. The discharge into waters will be heavily weighted by the Aroclors used as hydraulic fluids and lubricants and is therefore likely to have included a mixture of Aroclors 1242 to 1260. The residual in dumps will have a large fraction of the Aroclor 1242 production.

Rates of Transport within the Environment

The modes of transport of the PCBs within the environment are complex. Vaporized PCBs will be partially adsorbed on particulates, transported with the prevailing winds, and deposited on land or water by particle sedimentation or rain-out. PCBs introduced into water streams may be adsorbed by the waterborne particulates or the benthos; the adsorbed PCBs will diffuse into the bottom sediment, redissolve in the water stream or be entrained with sediment eroded from the bottom surface.

The problem is further complicated by the assimilation, transport and degradation of PCBs by the biota. A major fraction of the PCBs discarded in dumps is encapsulated in sealed containers or plastic resins. The rate of loss from these will therefore be low until the confining material is degraded and the PCBs released. The PCBs will then slowly diffuse through the surrounding soil. In principle, the rates of transport may be calculated from knowledge of the physicochemical properties of the PCBs and the pertinent data on atmospheric conditions, particulate transport, hydraulic dispersion, bottom sediment transport, and biological degradation rates. At present, the data are too incomplete and the interactions between the different elements in the environment too complex to attempt a formulation of but the crudest of transport models. The similarity between the properties of the PCBs and DDT, summarized in Table 2, permits rough estimation of some of the otherwise unknown routes and rates of transport of PCBs from the corresponding information on DDT. In Fig. 4, a generalized model for the distribution and transport of the PCBs is outlined, without any indication of the transport down spatial gradients within the differ-

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Table 2. Comparative Physical Properties of PCBs and DDT (Ref. 9, 23, 84, 93)

Molecular weight		Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	DDT
	Range[a]	154-358	222-358	200-392	324-460	352
	Average	262	288	324	370	352
% Chlorine		42	48	54	60	50
Solubility[b] in H_2O (at 20°C ppb)		200	100	50	25 Est	0 7
Vapor pressure[b] at 38°C (mm, Hg)		10^{-3}	$3\ 7\times10^{-4}$	6×10^{-5}	2×10^{-7}	2×10^{-6}
Vapor pressure at 20°C (mm Hg)		10^{-4}	3×10^{-4}	$3\ 6\times10^{-6}$		$1\ 5\times10^{-7}$

[a] Based on constituents present in amounts of 1 percent or more.
[b] The high values of the solubilities and vapor pressures of the PCBs are a consequence of the heavy weighting given the lower chlorinated species
[c] Extrapolated

ent compartments of the environment An attempt is made in the following sections to estimate fluxes between and within each compartment.

Air Transport

The estimated emission of 1500 to 2500 tons a year of PCBs, mainly by vaporization and open burning, is expected to be concentrated in urban areas By analogy to DDT (17, 18) it is expected that most of the airborne PCBs will be adsorbed on particles Since roughly three quarters of total suspended particulates (TSP) in urban areas are of non-agricultural origin (19), and the emission of TSP within cities is of the order of 2×10^7 tons per year (20), this gives rise to a rough estimate of PCB level on urban particulates of 50 to 80 ppm.

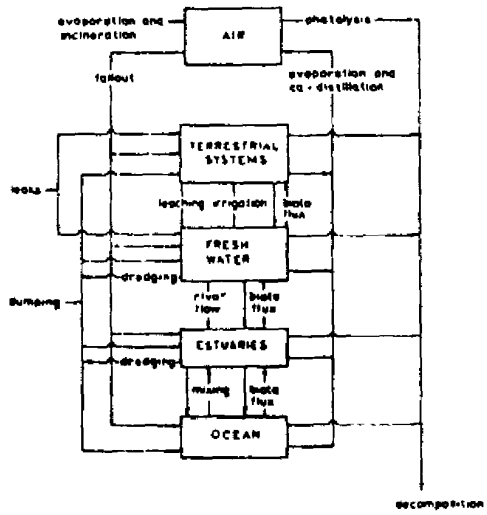

FIGURE 4. Environmental transport model.

The half-life of particulates in the air will depend greatly on the size of particles to which the PCBs are attached and the extent of atmospheric precipitation. (19) It is estimated that most of the vaporized PCBs will be deposited within 2 or 3 days, mostly onto the land mass and coastal waters surrounding urban areas. The small amounts of PCB attached to fine particulates will reside in the atmosphere for extended periods and be transported to remote areas

Based on the above assumptions, the rate of terrestrial net input of PCBs by aerial fallout in North America will be a little less than the rate of vaporization, about 1000 to 2000 tons/year The vapor pressure of Aroclor 1254, the dominant airborne contaminant, is close to that of DDE (21), and it is estimated, by analogy to DDE (17) that the likely half-life of PCBs in soil is of the order of five years The PCBs removed from the soil

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will become adsorbed to particulates, mostly of relatively short range, and be redeposited and vaporized one or more times until they reach the coast. By analogy to DDE (1, 2), the redistribution of PCBs by this mechanism is expected to have resulted in the redeposition into the ocean of one quarter of the PCBs that originally fall out in the terrestrial environment. The deposition pattern will be influenced by the size distribution of particles to which the PCBs are attached, with a major fraction ending in coastal waters and a small amount being transported into remote regions.

It is expected that a negligible fraction of the PCBs reaching the oceans will be revaporized; their concentration will be too low.

Water Transport

On account of the low water solubility and high specific gravity of PCBs, it is expected that most of the PCBs discharged into the environment will be resting as sludges or adsorbed in the sediment at the bottom of rivers or lakes near their point of discharge, and that transport in streams will be primarily by means of waterborne particles. Evidence for this postulate is indirect, consisting mainly of the strong adsorption of PCBs by surfaces (22), the observation of PCB concentrations as high as five times the solubility limit (6), and the evidence that chlorinated hydrocarbon pesticides are removed from contaminated lakes by adsorption in sediments and codeposition with algal bloom (24).

The transport of PCBs within rivers is as described previously, by solution and readsorption in the sediment and by sediment transport. The data on partition coefficient between sediments and water and on diffusivity in bottom sediment are not available so that the transport models (25) developed for rivers cannot yet be applied. The only measurements reported on PCBs in ground sediment are for Escambia Bay (6, 26). The PCB concentration in the sediment 10 miles downstream from a discontinued source of PCB loss was found to remain constant over a year suggesting that the PCBs are strongly adsorbed to sediment.

The amount of PCBs transported to the ocean in solution or suspension in river water is estimated as 200 tons/year (49), a small amount compared to the estimated input into rivers. Irrigation waters amount to about $\frac{1}{3}$ of the total river flow and are expected to carry a correspondingly lower amount, about 15 tons/year, of PCBs to the terrestrial environment.

Dredging and Dumping

Dredging of inland rivers and harbors may lead to significant transfer of PCBs from contaminated sediments, especially when the dredge spoils are dumped at sea. According to the Council on Environmental Quality (27), some 13×10^6 tons of polluted dredged spoils are dumped at sea annually off the United States, 90% off the Gulf and Atlantic coasts. A high figure for PCB levels in polluted sediments is 30 ppm, the highest level recorded in the Escambia Bay incident away from the immediate vicinity of the discharge (26). If all the polluted dredge spoils were contaminated to this level, the total rate of transfer of PCBs to the oceans would be around 400 tons/year, mostly into the Atlantic Ocean and Gulf of Mexico. Based on the general level of contamination a more reasonable estimate of rate of transfer would be only 20 tons/year.

Biota Flux

The total quantity of PCBs stored in migratory animals is very small (see below), and their movements cannot account for a significant fraction of environmental transfer of PCBs. The movements with the greatest local significance are probably the migrations of seabirds from the northern to the southern hemisphere; these might account for the movement of about a ton/year (28). Human fishing is estimated to remove only 1–2 tons/year from the eastern North Pacific, the western North Atlantic and the Great Lakes (30).

Separation and Transformation of PCB Isomers in the Environment

There are three processes by which the compositions of PCB mixtures may change after release into the environment.

Fractionation

In general, the water solubilities and vapor pressures of PCB isomers decrease with increasing

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Table 3 Percent Loss in Area of Seven Chromatogram Peaks of Aroclor 1254 After Steam Heating for 25 and 60 Minutes. [From Ref. 23]

Peak	25 Minutes	60 Minutes
1	66	83
2	41	74
3	22	73
4	40	54
5	14	51
6	0	15
7	0	33

chlorine content, although the decreases are not uniform (Table 2) (31) Hence the processes of evaporation, co-distillation and dissolution in water are expected to fractionate mixtures of PCBs, the lower isomers being much more mobile This has been confirmed for co-distillation by the results of Freed (21, 23) (Table 3), which show that, after 60-min steam heating, the ratio of the first to the sixth of the seven major chromatographic fractions of Aroclor 1254 was reduced by a factor of 5. Thus environmental transport mechanisms involving these processes are expected to reduce the proportions of the lower isomers in environmental samples near to the point of release, and to augment them in samples from remoter areas.

Photolysis and Chemical Decomposition

Photolytic decomposition of certain PCB isomers has been reported by Risebrough et al. (32, 33), and Safe and Hutzinger (34, 35) The results of the latter suggest that in natural sunlight some higher isomers are more easily broken down than the lower isomers (35). Hence photolysis is expected to reduce the proportions of at least some of the higher isomers. Photolytic dechlorination is also expected to give rise to lower isomers, including some which may not be present in commercial mixtures (35).

Because of their high stability in industrial use, we assume that other forms of chemical (non-biological) decomposition of PCBs are very slow in the environment.

Metabolism and Excretion

Published studies of the dynamics of PCBs in rats and birds (36–39) indicate that the higher isomers are generally taken up and or retained more efficiently In each case the proportions of pentachloro- and lower isomers found in the animals' tissues were generally lower than those in the Aroclor mixture to which they had been exposed, but there appears to have been little differentiation of the higher isomers except for one hexachloro-isomer (36–38) It is not clear in each case whether the deficiencies of the lower isomers resulted from metabolism or differential excretion, but it is likely that both occurred Because of their higher solubility in water (see above), the lower isomers would be expected to be excreted more easily than the higher isomers In one study on rats, loss of PCBs from the body was markedly retarded by administration of carbon tetrachloride (36), suggesting interference with metabolism in the liver In another study with rats, hexachloro-isomers were found in disproportionate amounts in the urine (37), suggesting that the tetra- and pentachloro-isomers were metabolized and the hexachloro-isomers excreted in part, while the heptachloro-isomers were differentially retained. Two studies of metabolism of PCBs in fish (40, 41) gave inconsistent results but showed no marked tendency for the higher isomers to accumulate differentially

Evidence from Environmental Samples

Veith (42) has found that the proportion of higher isomers increases downstream in some Wisconsin rivers and that certain isomers characteristic of lower Aroclors disappear Since the lower isomers are unlikely to be differentially retained in sediments (see above), this suggests that they are decomposed rapidly in the river environment Evidence of biodegradation of pesticides under anaerobic conditions (43) suggests the possibility that the degradation of the missing lower isomers may occur primarily by microbial metabolism in the bottom sediment We recommend that higher priority be given to this aspect of decomposition of PCBs.

A number of writers have reported that PCB samples extracted from animals generally match Aroclors 1254 or 1260, but that the lowest isomers are sometimes relatively deficient or missing, especially in animals high in food chains (38, 44) Since substantial quantities of Aroclors 1242 and

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Table 4. Relative Peak Heights in Gas-Liquid Chromatograms of Extracts from Sewage Sludges. [From Ref. 45]

Relative retention time	Sludge A	Aroclor 1254	Sludge B	Aroclor 1260
0 69	38	30	39	3
0 81	63	72	24	14
1 00	51	59	17	4
1 21	104	110	51	30
1 45	100	100	100	100
1 71	92	92	66	69
2 00	32	26	70	70
2 34	19	12	53	55
2 83	21	19	84	87
3 33	10	8	29	30
3 70	5	4	25	23

1248 must have been released into the environment (see above), these observations suggest that a large proportion of the lower isomers (those with 4 or fewer chlorine atoms) is missing from the animal samples. However, few critical data have been published. In one set of data from sewage sludge (45) (Table 4), none of the lower isomers is clearly deficient. In published chromatograms for birds (38, 46, 47) (Table 5), only the lowest isomers (tetrachlorobiphenyls) and one higher isomer were markedly reduced in comparison to Aroclor 1254. In human adipose tissue (46), however, pentachloro- and hexachloro-isomers were reduced or missing.

The higher isomer reduced in the bird samples (38, 46) is probably that reported as deficient in samples from the Gulf of California and Quebec and found to be degraded by ultraviolet light (32, 33). With this one exception, we conclude tentatively that higher isomers (pentachlorobiphenyls and higher) are not significantly differentiated as they pass through food chains up to fish and birds. Mammals appear to be able to excrete and/or metabolize penta- and hexachloro-isomers.

The lack of the lower isomers in samples from relatively contaminated areas could be accounted for either by metabolism or by their greater mobility. However, Risebrough and Berger (33) found that lower isomers were relatively deficient also in samples from fish in a remote lake in northern Canada. This suggests that differential metabolism is the primary mechanism in the environmental differentiation of isomers, outweighing the effects of differential photolysis and differential mobility, which would be expected to have reduced the proportion of higher isomers in remote samples.

Conclusions and Comments on Separation of PCB Isomers in the Environment

We conclude that most PCB isomers with four or fewer chlorine atoms have been degraded in the environment, possibly by microbial action. Decomposition of penta- and hexachloro-isomers appears to occur in birds and mammals, but this will have affected only a negligible fraction of the PCBs in the environment. Accordingly, we assume (3) that some 75% of the Aroclor 1242 released into the environment, 60% of Aroclor 1248, 20% of Aroclor 1254 and 5% of Aroclor 1260, have disappeared.

The above discussion has been confined to a general comparison of lower and higher isomers, because of the scarcity of data on relative proportions of individual isomers in environmental samples. In fact, the physical and chemical properties and biodegradability of PCB isomers depend on the positions of substitution as well as the total chlorine content. More precise data on the

Table 5. Relative Peak Areas (Peak 11 = 100) for Chromatogram of Extract of Eagle Carcass and Aroclor 1254. [From Ref. 47]

Peak No.	Relative retention time*	Eagle carcass	Aroclor 1254
1	0 39	7 5	6 8
2	0 49	34 8	100.0
3	0 53	55 0	42 3
4	0 58	15 7	21 0
5	0.70	68 6	191 5
6	0.79	28.0	32 2
7	0.83	111 9	127 5
8	0 97	68 7	66.5
9	1 04	91 6	105 2
10	1 23	92 5	139 5
11	1 46	100 0	100 0
12	1 72	62 2	75 5
13	2 01	28 7	23 6
14	2 32	18 4	42 6
15	2 86	32 6	38 8
16	3 38	15 4	22 2

* p,p'-DDE = 1 00

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exact quantities of individual isomers in environmental samples would permit more precise conclusions about the sources and routes of contamination We urge that numerical characterization of individual peaks should be published whenever possible

Cumulative Input into the Environment

From an extrapolation of the sales curve in Fig 1 to zero production in 1930, it is estimated that the cumulative sales in North America over the period 1930–1970 were 5×10^5 tons. Assuming that the proportions of sales for different uses were similar throughout the period, the cumulative losses may be estimated as about 3×10^4 tons into the air, 6×10^4 tons into fresh and coastal waters, and 3×10^5 tons into dumps and landfills Using the results of the previous section, it may be estimated that roughly one-third of the PCBs released into the air and one-half of those released into water have now been degraded It is difficult to estimate the extent of degradation in dumps, because some of the PCBs there may still be in sealed containers, but we assume in any case that leaching from dumps into fresh waters has so far been negligible.

Of the PCBs released into the air, we have assumed that most would have been adsorbed onto particulates soon after volatilization and would therefore have fallen out relatively close to the source. By analogy with DDT residues, PCBs in soil would be expected to have a half-life of the order of 5 years (2, 17) Again using the analogy with DDT and its metabolites, we may estimate that roughly one-quarter (1) of the total (i.e., 5×10^3 tons) will have been transferred into the sea, mainly into the Atlantic Ocean, and the remainder (1.5×10^4 tons) distributed over terrestrial North America, with a negligible fraction having fallen into fresh waters Other inputs to the sea are difficult to estimate but have probably been of the order of 10^4 tons (49). The remainder (2×10^4 tons) is assumed to have accumulated in lakes and rivers.

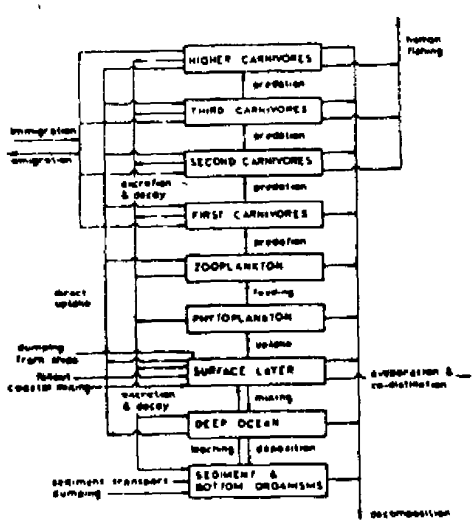

FIGURE 5 Ocean sub-model

Table 6 Range of concentrations of PCBs in samples from the Irish Sea and Firth of Clyde, Scotland October 1969 and subsequently (Ref 58). All figures are in ppm except those for seawater

	Sample size	PCB	Σ DDT*
Seawater	53	<10 ppt	<1-5 ppt
Zooplankton	7	0 01–0 03	0 01
Mussels	c 200	0 05–0 5	0 01
Norway lobster	33	0 01–0 1	0 01–0 1
Herring	154	0 01–2 0	0 01–1 0
Whiting muscle	18	0 01–0 4	0 01
liver	15	1 0–7 0	1 0–2 0
Cod muscle	6	0 3–1 8	0 4–0 52
liver	5	4 5–50	2 3–12
Other fish	83	0 1–1 0	0 04–1 0
Razorbill livers	7	2 –44	5 –13
Guillemot livers,			
birds found dead	49	2 –880	1 7–26
birds shot	5	0–2	0 1–0 8

* These figures, as given in the original source, include dieldrin as well as DDT and its metabolites, but dieldrin comprised only 4% of the total in the case of the guillemots

PCB Levels and Σ DDT/PCB Ratios in the Environment

In this section we compare the above estimates of cumulative input into the environment with measurements of PCB levels in physical and biological samples The purposes of this comparison are: (1) to use the observed distribution of PCBs in the environment to check the consistency of our

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Table 7. PCB levels in Swedish marine organisms 1965–68 [From Ref. 44]. Figures given are the mean (ppm in extractable fat), with range and sample size in parentheses; ΣDDT is the total of DDT and its metabolites.

	Baltic Sea				Stockholm Archipelago			
	Mean	Range	N	ΣDDT/PCB	Mean	Range	N	ΣDDT/PCB
Mussel	4 3	(1 9–8 6)	(40)	1 4	5 2	(3 4–7 0)	(15)	0 6
Herring	6 8	(0 5–23)	(18)	2 5	5 1	(3 3–8 5)	(4)	1 5
Seal	35	(16–44)	(3)	3.4	30	(16–50)	(3)	5 7
Guillemot eggs	250	(140–360)	(9)	2 3		—		
Heron					9400.		(1)	1 5
White-tailed Eagle:								
breast muscle					14000	(8400–17000)	(4)	1 8
brain					910.	(490–1500)	(3)	2 1
eggs					540.	(250–800)	(5)	1 9

models of environmental transport; (2) to define the types and locations of input to the environment which are responsible for the most serious contamination of the biota.

Uptake and Biological Magnification of PCBs in Food Chains

A large fraction of the reported measurements of PCB concentrations in environmental samples have been from animals, especially fish and birds high in marine food chains. Figure 5 outlines schematically a model for the transport of PCBs within a simple marine ecosystem. Laboratory experiments (6, 41, 55) indicate that aquatic invertebrates and fish can accumulate PCBs to levels between 3×10^3 and 7×10^4 times higher than those in the ambient water. It is not yet clear whether concentrations of PCBs are consistently increased as they pass up food chains from invertebrates to fish and from fish to fish (57). However, PCB levels are clearly magnified within food chains involving birds and mammals by a factor on the order of 10 to 100 at each step (32, 44, 56, 57, 58). Hence, in the long food chains characteristic of marine systems (59), the levels in the top predators may be 10^7 times higher than those in the ambient water (Tables 6 and 7). In extreme cases, such as the starved guillemots in Table 6, or the eagle fat in Table 7, the concentration factors may be as high as 10^8 or 10^9. Because of the extreme variability observed both within and between samples, it is difficult to use measured levels in animals as a direct measure of levels in the environment. However, it is possible to compare levels in the same species or in ecologically equivalent species to define spatial gradients in contamination (29, 44).

ΣDDT/PCB Ratios

Another approach (32, 56) utilizes the similarity in properties between the persistent PCBs and the persistent metabolites of DDT, primarily DDE. (In the remainder of this section, DDT and its metabolites DDE and DDD are grouped together as ΣDDT). Experiments suggest that PCBs and ΣDDT are accumulated by aquatic animals to an extremely similar degree from ambient water (41), and measurements in the same areas indicate that the ratios ΣDDT/PCB are very similar in animals from different levels in the food chain (Tables 6 and 7) (32, 56, 75). Hence the ratio ΣDDT/PCB in environmental samples, even in animals at the top of food chains, can be used to infer the ratio in the substrate, at least to order of magnitude (32, 56). Then the extensive information about the environmental distribution and transport of ΣDDT (2, 17) can be used to make inferences about the distribution and transport of PCBs.

Air

The only numerical measurements available of PCB levels in air are some estimates of levels in total suspended particulates (TSP) in four U S cities between 1968 and 1970 (E P A., unpublished data). The mean level of PCBs was about 50 ppm, with levels in one city substantially

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higher This is at least consistent with our earlier estimate based on rates of transport in the environment

Risebrough et al (60) were unable to detect PCBs in a sample of marine air off the California coast This suggests that long-range (inter-continental) transport of PCBs in air may be negligible

Land

We have estimated the cumulative net input into terrestrial North America as of the order of 1.5×10^4 tons For comparison, the total quantity of ΣDDT remaining in terrestrial North America is of the order of 3×10^5 tons, as estimated by two methods: total application minus estimated total losses to the sea (1); mean levels of 2–3 ppm in a wide variety of treated soils, and lesser amounts in untreated soils (2, 17, 61) Hence the continental mean ΣDDT/PCB ratio should be of the order of 20 However, PCBs are expected to be distributed primarily around urban areas and downwind from them, whereas ΣDDT is still concentrated in the agricultural and forested areas where it was applied (61).

A nation-wide monitoring scheme using starlings (*Sturnus vulgaris*) and woodcocks (*Philohela minor*) is in progress. Early results show mean PCB levels in pooled samples of fat from woodcock wings from eastern states in the range 4–7 ppm (62). ΣDDT levels from these pools are not yet available, but fat from woodcocks in Canada contains 6–130 ppm, depending on the local history of application (29) Woodcocks feed on earthworms and should be a good indicator for soil concentrations

Other data from terrestrial birds may be biased towards low ΣDDT/PCB ratios, because the birds were obtained in industrialized regions The median ΣDDT/PCB ratio in a small sample of terrestrial birds from California was 4 (32). Terrestrial birds of prey in five European countries have very high levels of PCBs, with ΣDDT/PCB ratios in the range 0.3–5 (63–67).

In human food, market basket surveys in the United States suggest a ΣDDT/PCB ratio of about 4 (68). Ratios in human milk (69, 70) and human blood plasma (71) are in the same range. However, except for sporadic instances of contamination, most of the human intake of PCBs appears to be in fish (68), whereas ΣDDT is much more widely distributed in the diet (72) If the fish and shellfish portions of the diet are excluded the ΣDDT/PCB ratio would probably be greater than 10 Similar data have been reported from Sweden, where the ΣDDT/PCB ratio in total diet samples and in human milk is about 7 (73)

Fresh Waters

Measurements of PCB levels in water are available only for relatively polluted rivers and bays and are summarized in note (50) Table 8 summarizes PCB levels and ΣDDT/PCB ratios in freshwater fish and birds PCB levels are both absolutely and relatively high in industrial rivers and in the Great Lakes, within the Great Lakes there is a gradient in ΣDDT/PCB ratios from west to east. Levels of PCBs are lower in the three samples from lakes in less industrialized areas listed at the bottom of Table 8 These data are consistent with our conclusion that most PCBs in fresh water systems result from local discharges by industries, but that there is also widespread aerial fallout of small quantities

Based on our assumptions of mean concentrations in fresh waters (50), we estimate that the water of the Great Lakes contains a quantity of PCBs of the order of 100 tons, the total quantity

Table 8. PCB Levels and ΣDDT/PCB ratios in North American Fresh Water Vertebrates

Area	Mean PCB level in fish (ppm)	ΣDDT/PCB ratio in fish and/or fish-eating birds	Reference
U S · industrialized rivers	1–213	0 005–0 35	55
Lake Ontario	19	0 08–0 2	55, 74
Lake Michigan	20	0 4–1	55
Lake Huron (Georgian Bay)	—	0 8	75
Lake Superior	—	2 4	75
Ontario Lake Nipigon	0 1	1–4	75
U S & Canada Prairie Lakes	<0 1	2	76
N. Quebec Lake Minto	0 1	1	33

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in other lakes would be negligible The quantity carried in river water would be only of the order of 3 tons. It is difficult to estimate the total quantity in the biota, but since the Great Lakes' fisheries probably remove less than a ton of PCBs per year (30), the total quantity in fish is probably only of the order of 10 tons. These quantities are negligible in comparison to the estimated cumulative input of 2×10^4 tons after allowing for degradation. Hence we conclude that almost all the PCBs that have been released into fresh waters are adsorbed onto bottom sediments There are no data to indicate the rate at which they are being released into water and into the biota or being biodegraded.

It is expected that PCB levels in ground water will be negligible, since any PCBs in water percolating through the soil should be adsorbed onto soil particles (77).

The Sea

According to our estimates, the total input of PCBs into the seas around North America has been of the order of 1.5×10^4 tons, mostly into the Atlantic Ocean, in part by localized discharge and in part by aerial fallout For comparison, the total input of ΣDDT into the oceans has been estimated as of the order of 5×10^5 tons (1), of which a disproportionate quantity, probably more than 10^5 tons, would have fallen into the North Atlantic Ocean, because of the heavy use of DDT in North America (17) Thus, on these arguments, the total quantity of ΣDDT in the oceans would exceed that of PCBs by several times, especially in the eastern North Pacific However, ΣDDT has been introduced over large areas (1, 2), so that it should be more uniformly distributed than the PCBs, the discharges of which are localized near industrialized coasts

Table 9. PCB Levels and ΣDDT/PCB ratios in Marine Vertebrates.

Area	Mean PCB level in fish (ppm)	ΣDDT/PCB ratio in fish, fish-eating birds and/or mammals	Reference
Long Island Sound	1 2	0.08–0.18	78
Bay of Fundy	0 5	0 4	29, 79, 80
Atlantic Ocean	0 1	0 2–0 6	57
Puget Sound	0 16	1 1	56
San Francisco Bay	0 1–1.2	1–3	32, 56
Californian Coast	0.02–1	5	32, 56
Gulf of California	—	10	32
Gulf of Panama	—	1–2	32
Pacific Ocean (Galapagos & Hawaii)	0 03	>10	56

Available measurements of PCB levels and ΣDDT/PCB ratios, summarized in Table 9, are generally consistent with these predictions, although the pattern is less clear than that in Table 8, in part because of the wide variability between species (cf. Tables 6 and 7). The highest PCB levels and the lowest ΣDDT/PCB ratios have generally been in areas close to industrial activity. At least in the Pacific, PCB levels decrease and ΣDDT/PCB ratios increase with increasing distance offshore. Data on marine birds summarized by Keith and Gruchy (29) show that these offshore gradients exist in both the Atlantic and Pacific, and show further that PCB levels in the Atlantic seabirds are 5–10 times higher than those in the same or ecologically equivalent species in the Pacific The correlation of high PCB levels with industrial activity has been demonstrated most clearly in Europe, where it has been observed along the coasts of Sweden (65, 81), the Netherlands (38) and Great Britain (82).

The only major discrepancy from this general picture is the observation (57) of extremely low ΣDDT/PCB ratios (of the order of 0 01) in zooplankton over a wide area in the North Atlantic Ocean. ΣDDT/PCB ratios in fish in the same area were of the order of 0.2 to 0.5. It is almost inconceivable that aerial fallout of PCBs could have exceeded that of ΣDDT by such large factors over such a large area; hence to explain the discrepancy, it is necessary to assume either selective removal of ΣDDT or a local source of PCBs. A likely local source is dumping or leakage from ships. PCBs introduced into the ocean in this way would frequently be mixed with oil, would tend to mix with surface slicks (83), and hence would be peculiarly subject to uptake by plankton Further study is necessary to confirm this suggested explanation or otherwise explain the anomalous low ΣDDT/PCB ratio in the Atlantic Ocean.

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Assuming the standing crop of fish in the eastern North Pacific to be of the order of 10^8 tons, and that in the western North Atlantic to be of the order of 5×10^7 tons (derived from 59), we may estimate the corresponding loads of PCBs to be of the order of 10 and 15 tons respectively. Assuming the standing crop of plankton to be five times larger than that of the fish (1, 2), the corresponding load of PCBs might be of the order of 100 tons. In the case of ΣDDT, it has been estimated that the total load in marine plants may be several times larger than that in marine animals (2); this may be true for PCBs also, but we know of no measurements to support it. In any case it seems unlikely that more than a few $\times10^3$ tons of PCBs are stored in the marine biota of the area considered, a very small fraction of the total quantity introduced. This fraction may be significantly greater than the corresponding fraction for ΣDDT (1), because of the extraordinarily high levels of PCBs in the zooplankton.

We know of no measurements of PCB levels in sea water. However, as in the case of fresh water, it seems likely that most of the PCBs would be attached to sediments or to floating particles. Observations on sediments (6, 26) are in accord with this.

As for ΣDDT, the deep oceans represent an ultimate sink for PCB residues. There is no information from which to estimate the rate of transfer of either to the deep oceans.

Summary and Conclusions

According to the estimates made in this paper, the PCBs released into the North American environment in the past are now concentrated in three major compartments in the environment: (a) buried in landfill dumps (roughly 3×10^3 tons, without allowing for degradation); (b) attached to sediments in rivers and the Great Lakes (roughly 2×10^4 tons); (c) attached to sediments on the continental shelf (roughly 10^4 tons). A further substantial quantity (of the order of 2×10^4 tons) has been widely distributed over the land and sea by aerial fallout and by disposal from ships. All the numerical estimates are expected to be valid to order of magnitude only.

Transfer of PCBs within the environment is expected to take place by the following main routes: (a) volatilization, aerial transport on particulates, and fallout, (b) leaching from dumps, (c) sediment transport in rivers and in the shallow sea; (d) sedimentation in the ocean. Uptake and transport by the biota is probably a quantitatively unimportant route of transfer of PCBs but is of major biological significance. Virtually no evidence is available on the rate of transport by any of these routes, but it is expected that all are very slow. In particular, PCBs in sediments in rivers and lakes are likely to move downstream and augment those in the shallow sea for a long period into the future.

As a result of Monsanto's restrictions on distribution, several inputs into the environment are likely to have been sharply reduced. As existing products containing PCBs are scrapped, the remaining inputs into the North American environment are expected to decline gradually over a period of the order of ten years.

As in the case of DDT and its metabolites, the total quantities of PCBs accumulated by the biota are an extremely small fraction (less than one percent) of those in the environment. This raises the possibility that the dissemination of relatively small fractions of the PCB production into sensitive areas may be primarily responsible for locally high levels of contamination of the biota. Evaluation of the long-term effects of the accumulation of PCBs and of the change in use patterns and production will require the development of environmental transport models more sophisticated than those currently in use, together with the requisite data.

The following aspects of environmental transport of PCBs should have high priority for future research:

1. *Properties and Rates.* Data are needed on the solubilities and vapor pressures of individual isomers; on the partition coefficients between water and sediments, water and fats; on the rate of photochemical decomposition and aerobic and anaerobic biodegradation; diffusion coefficients in sediment.
2. *Routes.* The magnitude of leaching from dumps and aerial transport of PCBs must be established by direct measurements of concentrations in ground waters, airborne

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particulates, and rainfall Data are needed on the magnitude of industrial losses in the past.

3 *Transport Models.* Data are needed on the transport of PCBs in contaminated sediments in rivers and shallow seas, including the dynamics of uptake from shallow sediment and losses to the ocean floor

4 *Levels* Additional data, including quantitative evaluation of the fractionation of isomers, are needed for fresh waters, soils, terrestrial plants and animals.

5 *Bioaccumulation model.* Inasmuch as the period since the first commercial application of PCBs is less than the lifetime of a number of species, including man, and the use and discharge pattern has been variable, there is a need to project the long-range impact of the PCBs on the different elements of the ecosystem.

Emphasis should be on coordinated approaches to sampling and modelling rather than a statistical accumulation of data.

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13. Approximately 190×10^6 tons of municipal waste and an equivalent amount of industrial solid waste are disposed of annually in the U.S.A., mostly in dumps Some 4.7×10^6 tons of industrial solid waste are dumped at sea (27) Of the remainder, 18×10^6 tons are burned in municipal incinerators, 14×10^6 tons in commercial incinerators, and 14×10^6 tons in open-burning dumps (14) Emission of PCBs from these sources may be gauged indirectly from measurements of the emission of combustible matter and polynuclear aromatics. From measurements reported by A. D

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Little (15) and Hein and Engdahl (16) it is estimated that 0.25 percent of solid waste is emitted by municipal incinerators and up to 20 percent by open burning. If it is assumed that the fraction of PCBs in the organic matter evolved from these sources is equal to the fraction of PCBs in the solid waste, the rate of emission of PCBs will be of the order of two tons per year from municipal incinerators and 200 tons/year from open burning dumps. Commercial incinerators and burning of automobile components each contribute a total quantity of polynuclear aromatic compounds (a rough gauge of incomplete burning) similar to that emitted by open burning (14). The estimate of 200 tons/year of PCBs from the burning of commercial waste and auto components is based on the relative magnitude of combustible pollutants from these different sources, weighted by the estimate of the fraction of total PCB production disposed of in open dumps. These estimates are highly speculative but are considered sufficient to discount the burning of wastes as the major source of PCB emissions.

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Accumulation of Polychlorinated Biphenyls in Ecosystems

by Robert W. Risebrough and Brock de Lappe*

Chlorinated biphenyl compounds have become ubiquitous components of the global environment They were first detected in species of Swedish wildlife (1, 2, 3) and were subsequently found in seals from the North Atlantic (4), in a bird of prey in Great Britain (5), in fish and birds from the Netherlands (6), and in both terrestrial and marine species of wildlife in western North America (7) In the Arctic they are present in the polar bears (*Thalarctos maritimus*) of Hudson Bay (8) and in fresh-water fish of tundra lakes that receive no pollutants save those that are present in the fallout from the atmosphere (9). In the Southern Hemisphere, they were found in all bird species analyzed that inhabit waters north of the Antarctic Convergence but could not be detected in a number of samples of wildlife resident in Antarctica south of the Convergence (10). In this paper some of the available residue data are summarized within the framework of a preliminary formulation of a mass balance equation for the global distribution of polychlorinated biphenyls

Commercial manufacture of PCBs was begun in the United States in 1929 (11), and environmental input may be assumed to have begun at that time. Current levels of PCBs in major sinks, such as the oceans, are evidently a function of many parameters, including the proportion of the total amount of PCBs produced over the past forty years that has so far entered the environment, pathways of dissemination, rates of degradation to other compounds, partition coefficients between water and lipid fractions of organisms and the rates of permanent deposition in the sediments. The determination of accumulation rates in major sinks and the prediction of levels to be expected in the future, given estimates of global production and of environmental input, constitute a challenging problem in environmental science.

A mass balance equation that would predict future levels of PCBs in the sea might profitably be modeled on the approach recently used by Weiss et al. (12) in considering the amount of mercury introduced to the sea as a result of the activities of man. Like PCBs, mercury in its various chemical forms is not essential to organisms but may be accumulated by them. Both groups of compounds move through the environment by water and air transport and are mobilized from pools that exist in a variety of industrial products, in addition to the pool of mercury in the earth's crust The transfer of mercury from the continents to the oceans in river runoff was estimated to be at most 2.8×10^9 grams per year, considerably less than the estimated rate of exchange between the continents and the atmosphere, between 2.5×10^{10} and 1.5×10^{11} grams per year. The latter figures were obtained from measurements of mercury in rainwater of the 1930's and in uncontaminated glacial ice. The amount of mercury produced by man per year is currently on the order of 10^{10} grams, of which one third was estimated to enter the atmosphere. Other sources of atmospheric mercury include the burning of fossil fuels, cement production and mining operations, but the integrated input resulting from man's activities in industry and agriculture was less than that released into the atmosphere by natural processes The doubling of the mercury content in dated layers of snow from a Greenland

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ice sheet over the past several decades was attributed to an increased disturbance of sedimentary rocks as a result of human disturbance (12)

Such an approach yielded the prediction that the current mercury content of marine organisms is at most no more than double that present in pre-technological times (12).

The only synthetic pollutant for which a comparable mass balance approach has been formulated is the insecticide DDT, together with its derivatives (13) Over the past fifteen years about 6×10^{10} grams per year of DDT have been manufactured in the United States, of which a considerable fraction is exported. The total global production per year was estimated to be in the order of 10^{11} grams (13), of which all may be assumed to be released into the environment. Analyses of DDT concentrations in river waters indicated that only a small fraction of the DDT applied to the land would reach the sea by river transport. The few data available for DDT concentrations in precipitation indicated, however, that as much as one quarter of the global production and use could be transported to the sea through the atmosphere (13, 14). Yet the total amount of DDT compounds estimated to be in pelagic marine organisms was only 10^9 grams. Evidently additional measurements of DDT in marine precipitation and in the water and organisms of the mixed layer are required before the mass balance approach can be used to predict future levels of DDT compounds in the oceans.

The ubiquity of the PCB compounds and their relatively high concentrations in marine organisms of certain areas require that an approach now be made toward the formulation of a mass balance equation in the global environment, as a necessary step in the implementation of a program that would prevent the buildup of unacceptable levels.

At the request of a number of environmental scientists concerned about the possibility that PCB levels would continue to increase in the sea, the Monsanto Company has recently released the total production figures for their Aroclor PCB products from 1960 through 1970, with estimated figures for production in 1971. Total U.S. production of the combined total of all PCB products rose steadily between 1960 and 1970, from approximately 2×10^{10} grams in 1960 to approximately 4×10^{10} grams in 1970. Estimated production figures for 1971, however, show a sharp drop from those of 1970 and are equivalent to 1960 levels Approximately half of this amount is used in "closed system" applications as electrical insulating liquids The domestic sales for all other uses, including heat transfer systems, hydraulics and lubricants, plasticizers, etc, rose from approximately 5×10^9 grams in 1960 to about 1.5×10^{10} grams in 1970, but estimated sales in 1971 were far below the 1960 figures A considerable fraction of PCBs used in the "open system" applications can be expected eventually to enter the environment. U.S export sales showed approximately no change between 1960 and 1965 and were in the order of 2×10^9 grams per year, but have since risen to about 5×10^9 grams (15) Of the other industrialized countries that produce chlorinated biphenyl compounds, notably France, Germany, Italy, Japan, and the Soviet Union, production figures are apparently readily available only from Japan where PCBs are manufactured by two companies, the Kanegafuchi Chemical Industry and the Mitsubishi-Monsanto Chemical Company, with combined production figures on the order of 10^{10} grams per year, somewhat less than the estimated 1971 total U S production of 2.0×10^{10} grams. In 1970, 60% of the PCBs produced in Japan were used for insulating fluids of capacitors and transformers, 15–20% for the solvent in carbonless reproducing paper, 10% for heat-transfer media, and 5–10% as plasticizers and for export (16).

The figures made public by Monsanto were for total PCB production only. The chlorine composition of the PCBs detected in marine systems may vary widely between that in waste water outfalls and in the tissues of fish-eating birds (17, 18). It is therefore essential to have production figures for each class of PCBs in order to understand PCB movements into and through marine ecosystems. These have been presented in the previous paper.

Combined U.S. and Japanese figures for 1970 were, therefore, on the order of 5×10^{10} grams A reasonable estimate for global production figures, including the PCBs manufactured in the Soviet Union and Western Europe, is therefore on the order of 10^{11} grams per year, equivalent to those of DDT.

Few data are yet available that permit calcu-

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lations of the amounts of PCBs transferred to the sea. Holden (19) found that about one ton of PCBs per year was entering the estuary of the Clyde as a component of crude sewage sludge from the Glasgow district. Approximately a ton of PCBs was also entering the estuary of the Thames as a component of sewage sludge from London. Comparable amounts of PCBs were found to be entering the Pacific Ocean from each of several waste water outfalls in California (17). The evidence for atmospheric dissemination of PCBs derives from their virtually universal distribution in the global environment, including resident Arctic species (9) and from the detection of PCB peaks in all samples of rain water obtained over a year at seven widely distributed sites in Great Britain (14). These PCBs were not quantitated. Permanent snow fields provide a historical record of PCB deposition with time. The possibility therefore exists for measuring the total amount of PCBs transferred from the atmosphere to snow fields receiving fallout from the major wind systems.

Measurements of PCB concentrations in the mixed layer of the ocean or in deeper waters have not yet been made. Concentrations in collections of zooplankton from the Atlantic, however, are surprisingly high. Samples from eleven stations over the Continental Shelf and Slope areas east of the northeastern United States contained a median concentration of 57 ppm PCBs, with a range from 2 to 260 ppm, in the extractable lipids, defined as all materials extracted in a Soxhlet apparatus with 2:1 hexane:acetone. Median dry and wet weight concentrations were on the order of 2 and 0.2 ppm respectively. Comparable values were obtained in samples from two stations near Bermuda and from two stations in the South Atlantic in the wind path from the industrialized areas of Brazil. Concentrations of PCBs in two samples from the eastern South Atlantic were lower by an order of magnitude (20). Because of wide differences in the total mass of zooplankton per unit volume of water, the values obtained in analyzing zooplankton samples are an imperfect indication of the local burden of PCBs. Moreover, partition coefficients between PCB concentrations in sea water and in zooplankton might be expected to depend on the nature of the lipids and other nonpolar substances in which PCBs accumulate.

Quantitation procedures for PCBs have not yet been standardized. In many waste water and biological samples, however, the profile of PCB peaks closely matches one of the commercial preparations, and accurate quantitation can then be made using the height of any one of the prominent peaks. The Atlantic zooplankton and fish samples from Long Island Sound (21) had a PCB composition that closely matched that of Aroclor 1254. Other environmental samples, particularly birds (10, 18), frequently have a PCB composition that is intermediate between 54 and 60 per cent chlorine. An arbitrary decision must therefore be made which may affect the values obtained by a factor as much as 2 or more. Most of the PCB values reported in papers from our laboratory have been obtained by comparing the total area of all PCB peaks emerging after p,p'-DDE to the total areas of the same peaks in chromatograms of the Aroclor 1254 standard. These values may be somewhat too high. Samples may contain a lower proportion of the PCB compounds with fewer chlorine atoms than does the 1254 standard. Also, the biphenyl molecules with more chlorine atoms have a greater ability to capture electrons and give, in general, proportionately greater responses in the electron capture detector per molecule of biphenyl. Thus, two eggs of the Common Tern, *Sterna hirundo*, from the colony on Great Gull Island, Long Island Sound, were quantitated for PCBs using two different methods. The areas of PCB peaks emerging after DDE were first compared with the 1254 standard and concentrations of 308 and 214 ppm in the egg lipids were calculated, respectively. When areas were compared with the total areas of the same peaks in chromatograms of the Aroclor 1260 standard, the PCB values obtained were lower by a factor of 2 and were, respectively, 145 and 98 ppm. The column used in this instance was 5% QF-1 on Chromosorb W, 80–100 mesh, acid washed, HMCS treated. Under the conditions employed, the integrated areas of all peaks of chromatograms of equal amounts of Aroclor 1242, 1254, and 1260, respectively, increased in the ratio 1.00:1.68:2.46 (22).

The different quantitation procedures used by various laboratories may be expected to yield, therefore, somewhat different estimates of PCB concentrations. It is reasonable to assume, how-

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Table 1. PCB in Marine Fish and in Fish from an Arctic Tundra Lake.

Locality, reference	Species	ppm, fresh weight	ppm, extracted lipid or fat
Tokyo Bay	Sea bass *Lateolabrax japonica*	1 7–3 4	120
Nova Scotia Banks (23)	Atlantic salmon *Salmo salar*	0 45	—
	Atlantic herring *Clupea harengus*	0 32–0 54	—
	Atlantic mackerel *Scomber scombrus*	0 35	—
	Cod *Gadus morhua*	0 02	—
Swedish West Coast (2)	Cod *Gadus morhua*	0 02	7 3
	Fish oil	—	0 7
Baltic Sea (2)	Atlantic herring *Clupea harengus*	0 27	6 8
	Cod *Gadus morhua*	0 03	11
	Atlantic salmon *Salmo salar*	0.30	2 9
	Fish oil	—	3 5
North Atlantic (24)	Flying Fish *Cypselurus exsiliens*	0 001–0 007	0 4–0 5
	Dolphin *Coryphaena hippurus*	0 01	10
	Shark (liver) *Carcharhinus longimanus*	0 3	0 6
	Mesopelagic Fish *Chauliodus danae* 800–900 meters	0 01–0 06	1 5–7 3
Long Island Sound (21)	Atlantic round herring *Etrumeus teres*	1 2	30
	Atlantic silverside *Menidia menidia*	3.2	52
	Atlantic mackerel *Scomber scombrus*	1 2	79
California Coastal Waters (25)	Northern anchovy *Engraulis mordax*	1.0	—
	Jack mackerel *Trachurus symmetricus*	0 02	—
	Bluefin tuna *Thunnus thynnus*	0 04	—

Table 1—Continued

Locality, reference	Species	ppm, fresh weight	ppm, extracted lipid or fat
Peruvian Coastal Waters (26)	Sardina peruana *Sardinops sagax*	0 01	0 6
	Caballa *Scomber japonicus*	0 02	2 0
	Bonito *Sarda sarda*	0 01	0 5
	Tiburón azul *Prionace glauca*	0 08	11 4
Lake Minto Ungava, Quebec (9)	Lake trout *Salvelinus namaycush*	0 04–0 6	1 1–12 0

(—) = Concentrations in parts per million

ever, in comparing these results, that differences of an order of magnitude would yield useful information on geographical distribution

In Table 1 are summarized some of the reported PCB residue data in fish from representative areas of the oceans and, for comparison, PCB values obtained in lake trout, *Salvelinus namaycush*, from a remote Arctic lake Among these, highest concentrations were in the fish from Tokyo Bay and from Long Island Sound (Table 1) These bodies of water can be expected to receive significant amounts of PCBs from urban sewage outfalls. A comparison of the residues in three species, the Atlantic salmon, *Salmo salar*, the Atlantic herring, *Clupea harengus*, and cod, *Gadus morhua*, from the Nova Scotia banks and from Swedish waters shows that both areas have comparable levels of PCB contamination. That PCBs have penetrated below the mixed surface layer of the North Atlantic is shown by their presence in fish characteristic of deeper waters obtained at depths between 800 and 900 meters PCBs were also detected in the fish from the coastal waters of Peru. The levels in lake trout from Lake Minto in the Arctic region of Quebec were higher than expected. Lakes in this area are shallow with rocky bottoms, almost no vegetation, and very low amounts of organic matter. It is interesting that levels in the Atlantic herring, a fatty fish, from both the Nova Scotia banks and the Baltic

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Table 2. PCB residues in petrels and shearwaters. Mean arithmetic concentrations in parts per million.

Species, reference	Breeding area	Non-breeding area	Tissue (N)	ppm, fresh weight	ppm, liquid lipid
Ashy Petrel (27) *Oceanodroma homochroa*	California coastal waters	California coastal waters	Whole body (9)	21	200 (120–320)
			Egg (6)	37	240 (130–370)
Leach's Petrel (28) *Oceanodroma leucorhoa*	Baja California, Pacific Coast	Eastern Pacific	Egg (1)	—	350
Black Petrel (7) *Loomelania melania*	Gulf of California	—	Whole body (8)	1 0	—
Least Petrel (7) *Halocyptena microsoma*	Gulf of California	—	Whole body (3)	0 4	—
Fulmar (7) *Fulmarus glacialis*	Alaska	Eastern Pacific	Whole body (3)	2 3	—
Pink-footed Shearwater (7) *Puffinus creatopus*	Chile	Western Mexico, northern Pacific	Whole body (1)	0 4	—
Sooty Shearwater (7) *Puffinus griseus*	New Zealand	Northern Pacific	Whole body (2)	1 1	—
Slender-billed Shearwater *Puffinus tenuirostris* (7)	Australia	Northern Pacific	Whole body (1)	2 1	—
Wilson's Petrel (10) *Oceanites oceanicus*	Hallett Station, Antarctica	Australian seas	Whole body (10)	2.1	11 0
	Palmer Station, Antarctica	North Atlantic	Whole body (9)	33	190
Giant Petrel (10) *Macronectes giganteus*	Palmer Station, Antarctica	Southern oceans	Egg (3)	0 2	3 5
Snow Petrel (10) *Pagodroma nivea*	Hallett Station, Antarctica	Antarctic ice-pack	Whole body (10)	0 08	0 3

were considerably higher, by an order of magnitude, than levels in the cod on a fresh weight basis, although the cod occupies a higher position in the food web. On a fat basis, however, residues in both species in the Baltic were comparable. These data suggest that amounts and kinds of lipids may affect the retention of PCBs, modifying the trophic accumulation predicted by the classical food chain concentration theory. Consistent with this hypothesis are the higher PCB residues measured in extractable lipids of the North Atlantic plankton than in the lipids of fish from the same area.

Table 2 includes a representative selection of PCB residues so far measured in species of petrels and shearwaters. These birds are strictly oceanic, rarely approaching land except to breed on islands or undisturbed coastal areas. They do not dive for their food as do the fish-eating species but rather feed upon plankton and other organic material obtained at the surface of the sea. Within a given marine ecosystem, their burdens of both PCB and DDT residues may be higher than those in fish-eating species such as the Brown Pelican, *Pelecanus occidentalis*, or the Osprey, *Pandion haliaetus* (7). Many species range widely, breeding in one hemisphere and spending the remainder of the year in the other. As expected, lowest levels were found in the Snow Petrel, *Pagodroma nivea*, a species resident in the Antarctic pack-ice region. High residues were found in tissues of the Wilson's Petrel, *Oceanites oceanicus*, from the population that breeds on the Antarctic Peninsula and migrates to the North Atlantic during the southern winter months. Comparable levels were found in the Ashy Petrel, *Oceanodroma homochroa*, a species that remains largely or entirely within the California coastal waters. High PCB concentrations were also found in an egg of a Leach's Petrel, *Oceanodroma leucorhoa*, obtained on the Islas Coronados, Baja California, Mexico, in the vicinity of San Diego, California (Table 2).

Table 3 summarizes the PCB data obtained from analysis of eggs of the Brown Pelican over a

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Table 3. PCB residues in eggs of the Brown Pelican, Pelecanus occidentalis, from North and South America. Mean arithmetic concentrations in parts per million of the egg lipid (30).

Breeding area	Sample size	ppm PCB, lipid
Peru	5	14
Panama	6	4
Venezuela	4	5
Jamaica	4	19
Florida, 4 colonies	87	71
Gulf of California	4	4
San Benitos, Western Baja California	10	39
San Martin, Western Baja California	6	72
Los Coronados	28	266
Anacapa Island, California	65	210

substantial portion of its range in both North and South America. This species feeds only upon marine fish obtained in coastal waters As expected, levels in the South American populations are substantially lower than those in North America. Concentrations in Florida tend to be about three times lower than those in California. This species does not occur along the coast of the heavily industrialized areas of the northeast United States, but in these areas the Osprey, another fish-eating species, may contain PCB residues five to ten times higher than those in the Florida populations of Brown Pelicans (29) The PCB or associated compounds are a possible cause of embryonic mortality observed in the Osprey populations of these areas (29).

The major difficulty in the design of a monitoring program to determine whether PCB residues are increasing or declining in a given sink is the lack of a statistical design that would establish how many individual specimens should be analyzed in order to determine the parameters of the pollutant distribution at a desired confidence level. Nor has it been established which species of organisms are most suitable for such monitoring programs. The distribution of residues of chlorinated hydrocarbon insecticides and their derivatives within a population is frequently non-Gaussian, although transformation of residue concentrations to their logarithms yields a distribution that is sufficiently Gaussian for the use of established statistical methods (31, 32) Confidence intervals, therefore, can be established for such parameters as the means of logarithms of residue concentrations The confidence interval however, cannot be transformed back to the original distribution There apparently are no satisfactory statistical methods that would determine the confidence intervals about the arithmetic or geometric mean of measured concentrations (32) Moreover, one hundred or more analyses of individual specimens might be necessary to determine the precision of the logarithm of the geometrical mean within a range equivalent to 10% of the value of the geometric mean (31, 32).

The two major research problems that are emerging from the occurrence of PCBs in the environment appear to be first, the determination of the accumulation rates in sinks, so that the concentrations found there might be related to input levels, and second, the determination of the effects of PCBs or their derivatives upon organisms and ecosystems at each contamination level. It might be hoped that a fraction of the considerable sums of money that would be spent at both national and international levels to "monitor" the environment will be diverted to programs designed to answer the significant questions rather than to assemble tables of random numbers, for which there is no pressing need.

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Contamination of the Bay of Fundy—Gulf of Maine area with Polychlorinated Biphenyls, Polychlorinated Terphenyls, Chlorinated Dibenzodioxins, and Dibenzofurans

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The procedure used to determine polychlorinated biphenyls (PCBs), polychlorinated terphenyls (PCTs), chlorinated dibenzodioxins, and chlorinated dibenzofurans is outlined in Table 1. It is based on the cleanup-chromatography of Holden and Marsden (1), modified as described (2). Most PCBs are eluted in fraction I. Fraction II contains some PCBs, p,p'-DDE, and PCTs, whereas heptachlor exposide, dieldrin, endrin, p,p'-DDD, and p,p'-DDT are eluted in fraction III. Fractions I and II are further chromatographed on alumina, essentially according to Porter and Burke (3), to determine chlorinated dibenzodioxins and dibenzofurans.

PCTs, hexa- and octachlorodibenzodioxin, and octachlorodibenzofuran were quantified by gas chromatography on 3% OV-210 on Chromosorb WAW 60/80 in a 6 ft × 4 mm column at 200°C. A 4% SE-30 column was used to quantify PCBs, chlorinated hydrocarbon pesticides, 2,3,7,8-tetrachlorodibenzodioxin, di-, tri-, and tetrachlorodibenzofuran.

Recovery of PCBs and chlorinated hydrocarbon pesticides in this procedure was generally better than 95% (2). Recovery of PCTs was 90%. Results of the analyses of commercial fishmeal, spiked with chlorinated dibenzodioxins and dibenzofurans are presented in Table 2.

PCTs were found only in eggs and fatty tissues of herring gulls in levels of 0.1 and 1.4 μg/g wet weight, expressed as Aroclor 5460, respectively. This indicates that PCTs are not as widely spread in the environment as PCBs.

Only a limited number of samples were analyzed for chlorinated dibenzodioxins and dibenzofurans. The samples included muscle and liver of white shark (*Carcharodon carcharias*), eggs of double-crested cormorants (*Phalacrocorax auritus*), and herring gulls (*Larus argentatus*), commercial herring oil, and groundfish herring fishmeal. No residues of chlorinated dibenzodioxins and dibenzofurans were found.

Detection limits of the individual compounds are estimated in Table 3.

The absence of chlorinated dibenzodioxins and dibenzofurans from aquatic animals is encouraging. However, these compounds are extremely toxic, and a more detailed investigation is necessary. The analytical technique should be further improved to achieve lower detection limits.

The levels of PCBs and chlorinated hydrocarbon pesticides found in fishes, double-crested

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Table 1. Procedure for determining PCBs, PCTs, chlorinated dibenzodioxins, and chlorinated dibenzofurans

Chromatography on alumina
(800°C 4 h, 5% H_2O)

Chromatography on Silicar[a]
(130°C overnight, 3% H_2O)

Fraction I (10 ml hexane)

Fraction I I (20 ml 2% CH_2Cl_2 in hexane) — PCB, C_6Cl_6

Fraction I II (10 ml 20% CH_2Cl_2 in hexane) — HCDD faster isomer, TCDD, OCDD, OCDF

Chromatography on alumina
(130°C overnight)

Fraction II I (20 ml 2% CH_2Cl_2 in hexane) — p,p'-DDE

Fraction II (20 ml hexane)

Fraction II II (10 ml 20% CH_2Cl_2 in hexane) — HCDD slower isomer, TCDD, CDF

Fraction III (10 ml 10% ether in hexane)

TCDD = 2,3,7,8-tetrachlorodibenzodioxin
HCDD, OCDD = hexa-, octachlorodibenzodioxin.
CDF = mixture of di-, tri-, and tetrachlorodibenzofuran
OCDF = octachlorodibenzofuran.

cormorants, and herring gulls from the Bay of Fundy-Gulf of Maine area are summarized in Table 4. The concentration of PCBs is generally higher than that reported for the same or similar species from other areas, such as the Baltic Sea (4), California coastal waters (5), Britain (6), and Western Canada (7).

It is interesting to note that the levels of PCBs found in fishes from the Bay of Fundy–Gulf of Maine area are about one order of magnitude higher than those in fishes from the Nova Scotia banks (2). Determination of PCB residues in Atlantic salmon (*Salmo salar*) also indicates that elevated levels of PCBs are associated with coastal areas. Thus muscle of salmon caught off Greenland contains 0.20 μg/g of PCBs, whereas in specimens landed in Canada PCB levels are from 0.45 to 0.62 μg/g on wet weight basis.

In all samples the peak pattern of PCB residues resembles quite closely that of Aroclor 1254, and the results are expressed as Aroclor 1254. However, fish from lower and intermediate levels of the food web contain relatively lower amounts of hexachlorobiphenyls (4th, 5th, and 6th major Aroclor 1254 peak) and higher amounts of tetra- and

Table 2. Analysis of spiked fishmeal samples, μg/g wet weight.

Sample	TCDD*		HCDD*		OCDD*	
	Added	Found	Added	Found	Added	Found
1	1.18	0.96	1.08	1.15	1.30	1.29
2	0.59	0.64	1.08	1.04	0.65	0.57
3	0.29	0.33	0.26	0.31	0.32	0.50

	CDF*		OCDF*	
	Added	Found	Added	Found
4	1.21	1.41	0.91	0.96
5	0.60	0.62	0.45	0.38
6	0.30	0.28	0.23	0.14

* See Table 1.

Table 3. Detection limits of chlorinated dibenzodioxins and dibenzofurans

Compound	Detection limit, μg/g wet weight
TCDD*	0.04
CDF*	0.02
HCDD*	0.02
OCDD*	0.01
OCDF*	0.01

* See Table 1.

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Table 4. PCB and chlorinated hydrocarbon pesticides in aquatic animals from the Bay of Fundy-Gulf of Maine area.

Species	Tissue	PCBs (as Aroclor 1254)	µg/g wet weight p,p'-DDE	Other
Herring *Clupea harengus*	whole fish	0 34	0 06	
Mackerel *Scomber scombrus*	muscle	0 35	0 07	
Plaice *Hippoglossoides platessoides*	muscle	0 38	0 01	
White hake *Urophycis tenuis*	muscle	0 44	0 03	
Ocean perch *Sebastes marinus*	muscle	0 32	0 03	
Cod *Gadus morhua*	muscle	0 55	0 04	
Sea raven *Hemitripterus americanus*	muscle	0 21	0 08	DDT 0 24
	viscera	0 73	0 30	
Basking shark *Cetorhinus maximus*	muscle	0 07	—	
	liver	1 07		
White shark *Carcharodon carcharias*	muscle	0 77	0 48	
	liver	218	335	DDT 63 DDD 43
Bluefin tuna *Thunnus thynnus*	muscle	1 54	0 15	
Herring oil		3 55	2 27	DDT 0 37
Fishmeal		0 54	0 19	
Double-crested cormorant *Phalacrocorax auritus*	eggs	43 5[a]	29 4[a]	
		17 2[a]	8 6[a]	
	muscle	3 38	8 40	
	liver	2 13	4 16	
	Subcut. fat	38	164	
	Abdom. fat	52	162	
Herring gull *Larus argentatus*	eggs	12 6[a]	5 67[a]	
		5 54[a]	2 83[a]	
	muscle liver	5 06	2 07	
		6 50	2 08	
	Subcut fat	75	26	

[a] Different nesting colonies.

pentachlorobiphenyls (1st and 2nd major Aroclor 1254 peak) than high trophic level white and silky shark (*Carcharodon carcharias* and *Carcharhinus falciformis*, respectively) and aquatic birds. Atlantic salmon parr fed Aroclor 1254-contaminated diet in the laboratory also contain relatively higher amounts of tetra- and pentachlorobiphenyls. This may indicate that fish more efficiently absorb the lower chlorinated bipbenyls. On the other hand, these compounds may be metabolized and excreted, so that a preferential accumulation of higher chlorinated biphenyls occurs in the food chains. The fractions of hexachlorobiphenyls at different trophic levels are summarized in Table 5.

The toxicological significance of environmental levels of PCBs and their rate of accumulation in the environment are not known. In spite of this, PCBs and other industrial halogenated hydrocarbons should be considered potentially harmful,

Table 5. Fraction of hexachlorobiphenyls at different trophic levels.

Sample	Fraction of hexachlorobiphenyls in terms of Aroclor 1254 peak heights,[a] $\frac{4+5+6}{1+2+4+5+6}$
Aroclor 1254	0 56
Fish, wild	0 38
Atlantic salmon parr on Aroclor 1254-contaminated diet	0 41
Silky shark	0 74
White shark	0.71
Eggs of double-crested cormorants and herring gulls	0 72

[a] Numbers refer to the major Aroclor 1254 peaks

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and their release into the environment should be limited as much as possible

Acknowledgments

We thank our colleagues at the Biological Station, St Andrews, New Brunswick, Canada, for samples of fish and Dr D Firestone, Food and Drug Administration, Washington, D C , U S A , for samples of chlorinated dibenzodioxins and dibenzofurans We thank Mrs. Madelyn M Irwin for typing the manuscript

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MONS 081359

Recent Fluctuations of Chlorobiphenyls (PCBs) in the Green Bay, Wisconsin, Region*

by Gilman D. Veith, Ph.D.†

Introduction

During the past six years, Wisconsin and Michigan have maintained a major stocking program for trout and salmon in Lake Michigan in an effort to re-establish a sport fisheries, and to control nuisance fish, such as the alewife. In 1969, Veith and Lee (1) found these large predators contained chlorobiphenyls (PCBs) at concentrations ranging from 10 to 25 μg/gm (fresh weight—as Aroclor 1254). Furthermore, the coho salmon eggs contained 12 to 17 μg/gm PCBs (fresh weight) which, based on the results of Johansson et al. (2) suggest that the PCBs may contribute to the poor reproductive success of the stocked fish in Lake Michigan. The seizure of fish from Lake Michigan, because of the presence of chlorinated pesticides and PCBs at concentrations greater than that regarded as safe for human consumption, has demonstrated that the continuous input of trace quantities of these chemicals may jeopardize major food resources for man, if proper management of hazardous chemicals is not practiced.

There are numerous examples of the aqueous transport of PCBs originating from industrial and sanitary wastes (3, 4). Veith and Lee (5) reported the presence of PCBs in sanitary wastes of all cities and villages studied in the Milwaukee River (Wisconsin) watershed. Dube (6) has found similar results in a study of PCBs in municipal wastes from southeastern Wisconsin. All of these data were obtained prior to or shortly after the voluntary partial ban on PCB sales by Monsanto Company. This paper presents the preliminary data from studies of the levels and sources of PCBs in rivers discharging into Lake Michigan—Green Bay in northeastern Wisconsin.

Green Bay (Figure 1) is an 120-mile long elongated bay in the northwest corner of Lake Michigan. The major rivers tributary to lower Green Bay are the Fox (mean discharge of 11×10^6 m^3 day^{-1}), which enters at the southwest end of the Bay, and the Oconto (2×10^6 m^3 day^{-1}). Peshtigo (2×10^6 m^3 day^{-1}) and the Menominee (9×10^6 m^3 day^{-1}), all of which enter along the northern shore of the Bay (7). The Fox and Menominee Rivers receive the wastes from the cities of Green Bay and Marinette (Wisconsin)—Menominee (Michigan), respectively. The Oconto River receives the wastes from Oconto Falls and Oconto, and wastes from the city of Peshtigo are discharged into the Peshtigo River. The Big Suamico and Pensaukee Rivers primarily drain agricultural and forested land and do not receive any major municipal wastes above the respective sampling sites.

Experimental Procedures

Field Sampling

The procedures used in this study have been discussed in detail elsewhere (5). The collection of water was conducted with all-glass systems to

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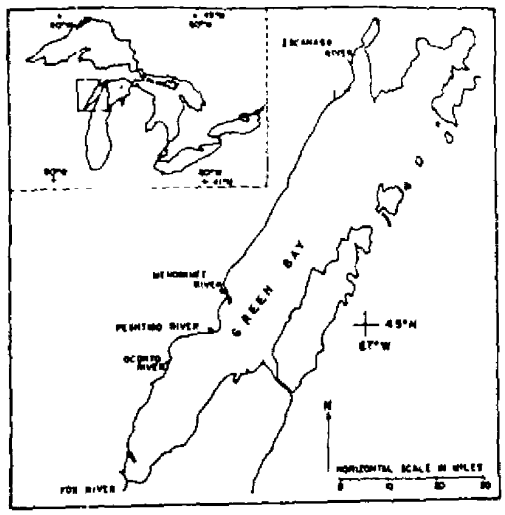

FIGURE 1. Location of Green Bay, Lake Michigan and major rivers tributary to the Bay

preclude possible interaction of the sample with rubber, plastic, or polyvinyl chloride surfaces. Samples were collected from the river by submerging a weighted, glass carboy (20 l) at a depth of 0.2 m in the center of the main channel. Preservatives were not added, as samples were cooled and extracted within 24 hours of collection.

Extraction

Water samples (20 l) were batch-extracted twice with hexane in 2 l separatory funnels. The hexane portions were combined, dried with anhydrous Na_2SO_4 and concentrated to 15 ml for cleanup in a gentle air stream.

Liquid Chromatography

The cleanup of extracts for gas chromatographic analysis was conducted with liquid chromatography on Florisil, as described by Reynolds (8) and Hughes et al. (9). The media (Kensington Scientific) was extracted in a Soxhlet extractor for 24 hours with an azeotrope of hexane and acetone (1:59) to remove organic impurities. The azeotrope was evaporated from the Florisil at 105°C, and the Florisil was heated to 650°C for 2.5 hours for activation.

The Florisil column for preliminary cleanup was prepared by vibrating 19 g of Florisil into a 25 mm o.d. glass column, which was fitted with a glass frit and Teflon stopcock. The column was topped with 10 g anhydrous sodium sulfate to prevent deactivation of the Florisil by traces of water in the extract. The extracts were placed on the column and eluted with hexane (200 ml) to recover the PCBs, if present. With some samples it was necessary to rechromatograph the hexane eluate from the 25 mm o.d. Florisil on a smaller diameter Florisil column (9 mm i.d.) to isolate the PCBs from organic interferences. If necessary, the PCBs were separated from the DDT group of pesticides through chromatography on silicic acid (10, 11).

Instrumentation

The analyses of water extracts were conducted on an Aerograph 1745–20 gas chromatograph equipped with concentric tube electron capture detectors (^3H, 250 mC) and a 50:50 effluent splitter for simultaneous analysis with electron capture and flame ionization detectors. Analytical GLC columns consisted of 2.0 m × 1.8 mm glass coils which were packed with either OV-101 (3 percent), OV-101/XE-60 (3·3 percent), or OV-101/QF-1 (3:4.5 percent), coated onto Gas Chrom Q (720/140 mesh). The carrier gas (purified N_2) was maintained at 21 ml min^{-1}; and the injector, column, and detector temperatures were 250°C, 180°C, and 220°C, respectively.

Analysis

The commercially prepared PCBs in the U.S.A. (Monsanto Company, St. Louis, Mo.) exist as seven complex mixtures under the name "Aroclor", which range in chlorine content from 21 to 62 percent. When the PCB mixtures are chromatographed with GLC, the mixtures of isomers produce both resolved and superimposed peaks and are somewhat characterized by the GLC fingerprint presented as relative peak heights and retention times. Because of the complexity of the mixtures, determinations have been quantitatively defined by comparing the area of a sample chromatogram to the area of a known quantity of the commercial mixture which most closely resembles that of the sample.

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Table 1 Variations of Chlorobiphenyls in Rivers in the Green Bay Study Area.

River	Concentration (μg/l as Aroclor 1254)[a]			
	12/29/70	5/21/71	7/20/71	8/6/71
Peshtigo River, Peshtigo	0 31	0 38	<0 01	<0 01
Oconto River, Oconto	0 45(3)	0 16	<0 01	<0 01(3)
Pensaukee River, Pensaukee	<0 01	<0 01	<0 01(1)	<0 01(1)
Big Suamico, Suamico	<0 01	<0 01	<0 01(1)	<0 01(1)
Fox River, Green Bay	0 18[b] (3)	0 26	0 16	0 15

[a] Mean of two analyses unless noted otherwise.
[b] Fox River samples analyzed as Aroclor 1248. Late eluting components present near municipal waste treatment outfall

Explicit chemical confirmations for the presence of PCBs in each sample were not possible in this study PCBs with similar retention volumes and relative peak heights were confirmed in the fish from the Milwaukee River using i.r. and mass spectrometry (5). The analyses do not preclude the possible presence of other chemicals which may have similar chemical properties, such as the chloronaphthalenes.

The recoveries of PCBs from water samples which were "spiked" with Aroclor 1254 and 1260 were approximately 80 to 85 percent Although the relative error at 1 μg/l was about ±8 percent, the relative error in replicate analyses of river waters at the 0.1 μg/l level may increase to 15 to 20 percent.

Results and Discussion

The results of the monitoring of five rivers in the Green Bay area for PCBs during 1971 are presented in Table 1. The concentration of PCBs in the Pensaukee and Big Suamico Rivers remained below the determinable limit of 0.01 μg/l throughout the period of the study. The PCBs in the Peshtigo River below the city of Peshtigo were approximately 0.3 to 0.4 μg/l (as Aroclor 1254) until May 21, 1971, but decreased to below the determinable limit by July 20, 1971. PCBs in the Oconto River below the city of Oconto were present at a concentration of 0.45 μg/l (as Aroclor 1254) on December 29, 1970, but decreased during the spring of 1971 and were also below the determinable limit on the July 20 sampling date. In contrast, no trends in the concentrations of PCBs in the Fox River were observed, and the levels were found to be above 0 1 μg/l (as Aroclor 1248) throughout the study It should be noted that the chromatograms of the PCB mixtures in the Oconto and Peshtigo Rivers were most similar to that of Aroclor 1254, whereas the mixtures in the Fox River were predominately Aroclor 1248, with minor components similar to those in Aroclor 1254 sometimes apparent.

The initial purpose in monitoring the tributaries of Green Bay was to relate the composition and concentration of PCBs in the major tributaries to those in the water from the Bay and to examine possible changes in the composition of PCBs in the sediments. The data obtained from the initial monitoring, which shows that the PCB concentrations in two of the major tributaries decreased sharply to below the determinable limit in 1971, suggests that the self-imposed restrictions on the sale of PCBs by Monsanto Company in 1970 and 1971 may be having an immediate effect in some river systems. Continued monitoring of the Fox River will be conducted to determine if the levels of PCBs arising from this highly industrial area will also diminish in the near future.

Although the analyses of water from Green Bay indicated the concentrations of PCBs varied from 0 07 μg/l (as Aroclor 1248) at Long Tail Point near the city of Green Bay to 0.04 g/l approximately 35 miles northeast of the city near Sturgeon Bay, the variations introduced by windmixing and the inability to measure small concentration differences below the 0.05 μg/l level may make it impossible to determine if the decline in PCBs in tributaries will be reflected in the water from the open Bay in the near future. Consequently,

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the sampling program has been expanded to include fish and other organisms of the Bay which contain μg/gm quantities of the PCBs

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MONS 081363

Polychlorinated Biphenyl Residues in Milk of Environmentally and Experimentally Contaminated Cows

by G. F. Fries*

Polychlorinated biphenyl (PCB)† residues have been found in the milk of cows. In some instances the residue levels exceeded the FDA guideline 0.2 ppm in milk (equivalent to 5.0 ppm in milk fat), and the milk was removed from the market. The major source of PCB residues in milk is Aroclor 1254 that has been used in coatings for concrete silos. Aroclor 1254 is unaltered in silos, and most of the contamination is adjacent to the walls (1, 2).

We have observed a number of farms with PCB-treated silos and have fed Aroclor 1254 to cows under controlled conditions. This paper summarizes our major findings.

Nature and Occurrence of Residues

The PCB recovered from silage is identical to standard Aroclor 1254 (1). However, many of the components with short gas chromatographic retention times do not occur in milk residues (Fig. 1). The components with short retention times are apparently less chlorinated than those with long retention times. Our observations in cows are similar to observations in other species (3).

A complication in analyzing environmental samples is a possibility of interference by DDT and some of its related compounds. We dehydrochlorinated the samples to remove possible interferences of DDD and DDT. DDE did not interfere, because those components of Aroclor 1254 with the same retention time as DDE did not occur in significant amounts in milk (Fig. 1).

We obtained milk tank samples from six farms with PCB-contaminated silos. The PCB levels in milk fat are summarized in Table 1. In all cases PCB concentration in milk fat exceeded the FDA guideline, at least part of the time, when silage was fed. When the silage was not fed, levels of PCB in milk fat were always lower than the guidelines.

The farms represent a variety of feeding and management conditions. The results suggest that any dairyman with a contaminated silo will probably exceed the guideline at least some of the time during the year. While a few higher levels have been reported for herds removed from the market, most were within the range of our observations. The number of farms with PCB-contaminated silos is not known. However, PCB contamination of milk is probably more prevalent than the regulatory record would suggest.

Comparison of DDE and PCB

We have observed a herd that was simultaneously contaminated with high levels of DDE and Aroclor 1254 from a silo. By a fortuitous set of circumstances, the cows had been removed from the sources of both contaminations at about the same time. A detailed description of this work has been prepared (4)

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† In this paper the term PCB is interchangeable with Aroclor 1254 or, in the case of milk and body fat, residues derived from Aroclor 1254.

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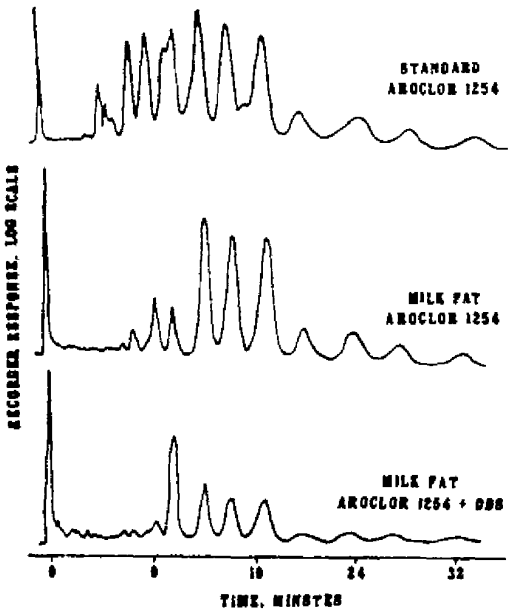

FIGURE 1 Gas chromatograms of Aroclor 1254 standard and residues in milk The 6 ft × ¼ in o.d column was packed with 10% DC-200 on Gaschrom-Q A 95% argon–5% methane mixture was used as carrier gas and the column temperature was 200°C

The average concentration of PCBs in milk fat was 19 3 μg/g when the silage feeding stopped. This concentration declined to 10.3 μg/g within three weeks We continued to sample the individual cows at three-week intervals for approximately four months. After three weeks the decline in concentration was linear, when plotted on semilog graph paper, suggesting first order kinetics

Table 1. PCB concentrations in milk fat from farms with contaminated silos*

Farm	11/10	12/7	1/21	3/24	5/11
			(μg/g)		
1	9 6	8 8	6 7	NS	7 0
2	7 5	5.7	6 7	6 6	*5 6*
3	NS†	*1 5*	7 4	5 0	*8 1*
4	NS	*2 0*	*1 4*	*1 4*	6 0
5	*3 5*	*2 7*	6 1	10 3	10 5
6	NS	*1 0*	6 2	*5 2*	*2 9*

* Silage was not being fed when italicized samples were obtained
† Not Sampled.

Table 2 Average rates of decline of DDE and PCB concentration in milk fat of cows in various stages of lactation*

Group	Cows	DDE	PCB
	(No)	(day^{-1})	(day^{-1})
Mid lactation	16	0 0145	0 0147
Early lactation	9	0 0107	0 0109
Late lactation	6	0 0147	0 0140
All	31	0 0134	0 0134

* The values are for the constant, k, in the linear form of the first-order equation $\ln C = \ln C_0 - kt$ where C is the milk fat concentration, C_0 is the initial concentration, and t is time in days Fitted by least squares

First-order rate constants were calculated for both DDE and PCBs for the individual cows A summary is presented in Table 2 The overall average of the rate constants for PCB was identical to that for DDE. The average DDE rate constant was similar to the rate that we have previously reported (5) There was a tendency for cows in early lactation to have lower rate constants than the other groups of cows.

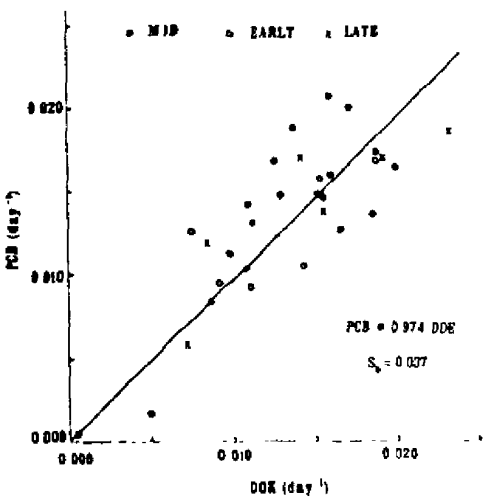

FIGURE 2 Relationship of the rates of decline of DDE and PCB concentration in milk fat of individual cow Mid, early, and late are stages of lactation (4)

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Table 3. Effect of phenobarbital and phenobarbital with activated carbon on the concentration of DDE and PCB in milk fat.[a]

Treatment	Cows (No.)	Concentration Initial (μg/g)	Concentration Final (μg/g)	Final/Initial	S.D.
		DDE			
Control	5	11.6	5.2	0.45	±0.05
Phenobarbital	10	9.5	4.3	0.45	±0.15
Phenobarbital+Carbon	6	8.0	3.7	0.46	±0.20
		PCB			
Control	5	19.3	7.4	0.38	±0.06
Phenobarbital	10	17.7	7.0	0.40	±0.11
Phenobarbital+Carbon	6	22.3	8.5	0.37	±0.14

[a] Observation period was 6 weeks. Phenobarbital was fed at 5 grams per day for the first three weeks and activated carbon at one kilogram per day for the 6 weeks.

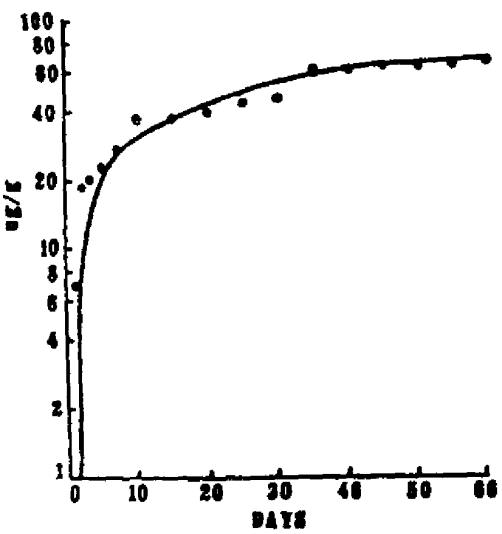

Figure 3. Concentration of PCB in milk fat of cows fed 200 mg/day Aroclor 1254 for 60 days. Each point is an average of nine cows.

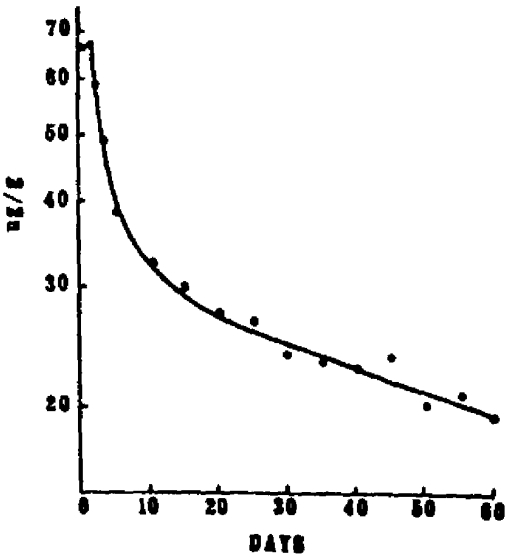

Figure 4. Concentration of PCB in milk fat after feeding Aroclor 1254 stopped. Each point is an average of nine cows.

Relationship of the rate constants for DDE and PCBs within individual cows is presented in Fig. 2. The correlation ($r = 0.82$) between the rate constants of the two compounds was significant ($P<0.01$). The usual linear regression was calculated, and the intercept did not differ significantly from zero (0). Therefore, the regression in Fig. 2 was recalculated, forcing the intercept through zero. The regression coefficient, 0.974, was essentially unity.

In some cases there was considerable variation between the rate constants for DDE and for

Table 4. Concentration of PCB in milk fat and body fat of cows fed 200 mg/day PCB for 60 days.

Time	Milk fat	Body fat
(days)	(μg/g)	(μg/g)
30	45.6±8.4[a]	21.9±8.5
60	66.7±8.4	44.0±12.2
90	24.0±3.0	40.3±6.4
120	19.4±2.4	28.8±6.2

[a] Standard deviation.

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Table 5. Normalized concentration of chlorinated hydrocarbon compounds in milk fat and body fat of cows after continuous feeding.[a]

Compound	Reference	Observations (No.)	Milk fat 20 days (μg/g)	Milk fat 60 days (μg/g)	Body fat 60 days (μg/g)
Aroclor 1254		9	0.20	0.33	0.20
DDE	(5)	3	0.21	0.29	0.23
	(7, 8)	12	0.27	—	—
Dieldrin	(7, 8)	12	0.19	—	—
DDD	(5)	3	0.063	0.077	0.046
p,p'-DDT[b]	(5)	3	0.036	0.049	0.033
	(7, 8)	12	0.036	—	—
	(9)	4	0.106	—	—
o,p'-DDT[b]	(9)	4	0.023	—	—

[a] Values are normalized to an intake of 1 mg/day
[b] Values are sum of DDD and DDT.

PCBs within a given cow. The rate constants for the two compounds within a given cow were tested statistically (6), but the differences were not significant.

The usefulness of phenobarbital alone, or in combination with activated carbon, in accelerating the reduction in milk concentration of DDE and PCBs was tested using three groups of cows. Neither phenobarbital nor phenobarbital in combination with activated carbon had an effect on the relative reduction in concentration of either compound (Table 3). We have previously reported a small effect of phenobarbital on DDE, but we did not consider it of practical significance (7). The absence of an effect here is consistent with that interpretation. The failure of activated carbon, even in combination with phenobarbital, to affect the reduction of DDE and PCB concentrations is consistent with our previous interpretation of laboratory experiments (8).

Aroclor 1254 Feeding Study

We have carried out a controlled feeding study using nine Holstein cows. The cows were fed 200 mg per day Aroclor 1254 for 60 days. Milk samples were obtained periodically during the 60-day feeding period and the subsequent 60-day period. Body fat samples were obtained by biopsy at 30-day intervals.

The cows were selected to have a range in both the stage of lactation and level of milk production. However, preliminary examination of the results indicates that there was little difference in the residue levels due to these factors. Therefore, only average data for all cows are presented.

The average level of PCBs in the milk fat during the feeding period is presented in Fig. 3. The standard deviation of any given point did not exceed ±10% of the mean. The concentration of PCBs increased rapidly and approached a "steady state" at about 40 to 60 days. As expected from our field studies, the shape of the curve is similar to that for other chlorinated hydrocarbon pesticides, particularly DDE (5).

The decline in PCB concentration in the milk for the 60 days after feeding stopped is presented in Fig. 4. This curve is quite typical of previous findings with DDE and was resolved into a two-component first-order system (5). The equation for the curve normalized to an initial concentration of 1.0 μg/g is:

$$C = 0.52e^{-0.25t} + 0.48e^{-0.008t}$$

Where C is concentration, e is the base of the natural logarithms, and t is days.

The constants are similar to our previous observations for DDE (5). While the rate for the second component in this study was less than the values found in the field, it was within the range of values that one might expect.

The level of PCB in body fat at various times is presented in Table 4. For reference purposes, milk fat levels at these times are also presented.

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While the PCBs were being fed, the level in milk fat was higher than that in body fat. When feeding stopped, milk fat levels dropped below and appear to reflect body fat levels.

We have conducted a number of studies with chlorinated hydrocarbon pesticides under conditions similar to those of this PCBs study. A summary of levels in milk fat at 20 and 60 days and body fat at 60 days with normalized intakes is presented in Table 5. The levels of PCBs are similar to levels of DDE and dieldrin in corresponding samples. In contrast DDD, p,p'-DDT, and o,p'-DDT are transferred to the body fat and milk fat at much lower rates than DDE and PCBs.

Conclusions

Farms having silos that have been treated with PCB-containing paints will frequently have residues of PCBs in milk which exceed the FDA guidelines. The behavior of this residue in the cows is similar to DDE and other chlorinated hydrocarbon pesticides resistant to metabolic degradation. The only practical countermeasures appear to be to decontaminate the silos sufficiently to remove most of the PCBs or to discontinue the use of these silos completely. Limited field experience and the similarity of PCBs to DDE suggest that there are no practical procedures to minimize the transfer of PCBs from the diet to the milk or to speed up the elimination of PCBs from cows.

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MONS 081368

Polychlorinated Biphenyls in Non-carbon Copy Paper

by Masanori Kuratsune and Yoshito Masuda*

In an effort to clarify the distribution of polychlorinated biphenyls (PCBs) in our environment, it was suggested by Dr. T. Hirayama, National Cancer Center, [Japan] that PCBs or their related compounds might be used for production of non-carbon copy paper. Three of 4 Japanese brands of the paper on the market were, therefore, collected and examined for PCBs. The paper consists of three different sheets, namely upper, middle, and lower ones. These sheets of paper were separately extracted with acetone in a Soxhlet apparatus for 3 days. The extracts were examined by gas chromatography with an electron capture detector, using 3 different liquid phases, namely 5% SE-30, 5% QF-1, and 2.5% DEGS coated on Chromosorb W AW DMCS. The gas chromatographic patterns observed were all identical with that of Kanechlor-300 (a commercial brand of PCBs) containing 43% of chlorine (Fig. 1). The infrared absorption spectra and mass-spectra of the extracts also demonstrated the presence of Kanechlor-300. The approximate concentration of PCBs was 2–3% in the upper and middle sheets and 0.02% in the lower sheets as shown in Table 1.

To estimate how much PCBs stick to fingers by handling the copy papers, a set of 96 precut sheets of the same size paper, consisting of 32 sheets of each of the upper, middle, and lower ones, was counted by turning over all the sheets one by one by fingers. After counting, the fingers were washed with n-hexane once and the resulting n-hexane washings were examined for PCBs. The amount of PCBs in the washings, calculated as Kanechlor-300, ranged from 11.40 to 52.68 μg in 5 subjects (Table 2). It was proved thus that PCBs in the paper easily stuck to fingers when handled. It was also demonstrated that only one third of the PCBs stuck to fingers can be removed by ordinary hand washing with soap and water (Table 2).

In addition to the above domestic brands of [Japanese] paper, a few other samples of non-carbon copy paper were analyzed for PCBs. One of them was a brand made by one of the leading paper makers in Britain and was obtained as packed in its original container in May, 1971. Analysis showed that both upper and middle

Table 1. Amounts of PCB in carbonless copying paper.

Brand	Kind of paper	Weight of paper (g/100 cm²)	Amount of acetone extract[a] (mg/g)	Amount of PCB found[b] (mg/g)
A	Upper	0.47	117.0	64.7
	Middle	0.56	125.8	63.8
	Lower	0.51	23.4	0.24
B	Upper	0.48	40.8	30.7
	Middle	0.55	37.8	26.0
	Lower	0.51	79.8	0.28
C	Upper	0.40	59.6	31.6
	Middle	0.53	61.0	22.2
	Lower	0.50	28.2	0.20

[a] Weight of extract per weight of paper.
[b] Weight of PCB calculated as Kanechlor-300 per weight of paper.

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sheets of this make contained PCBs. The second sample, which was of American make and obtained as packed in its original container in June 1971, also contained a considerable amount of PCBs. Another sample of paper, which was sent to us for examination by a company in Thailand however, did not contain PCBs. We were told that it is also of American make. A sample of non-carbon copy paper which was used by the U.S. Printing Office in 1967 was obtained from the American Consulate in Fukuoka and analyzed for PCBs. It also contained a large amount of PCBs.

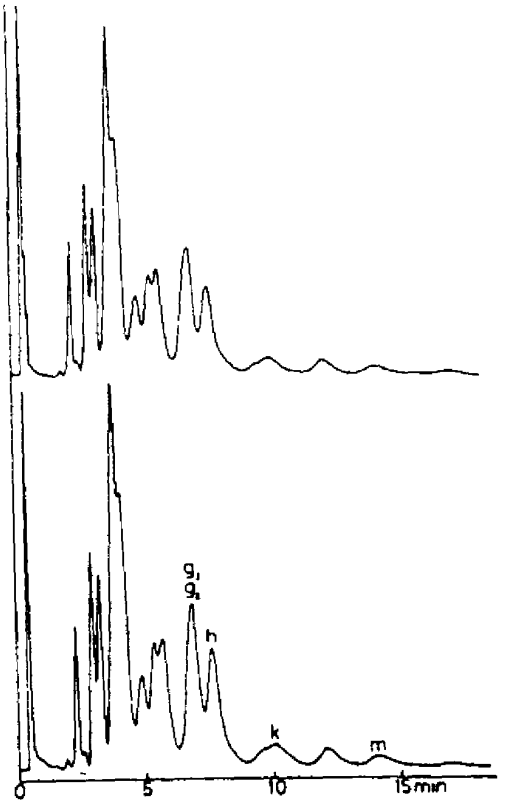

FIGURE 1 Gaschromatograms of kanechlor-300 (upper) and the acetone extract of copying paper (lower)
Column. Glass column (3mm×2m) containing 5% SE-30 on chromosorb W AW DMCS
Column temperature 195°C.

Table 2 Amounts of PCB found from fingers after contacting 96 sheets of paper

Subject	Amount of PCB*	
	Washed with acetone (μg)	Washed with acetone after hand washing with soap (μg)
1	29.76	16.31
2	12.60	10.47
3	11.40	4.30
4	52.68	17.74
5	44.65	29.15
Average	30.22	20.60
Standard deviation	16.60	13.11

* Calculated as Kanechlor 300

Needless to say, the free use of PCBs for this kind of very popular copy paper necessarily leads to the uncontrollably heavy, direct exposure of the general population to it. In view of its chemical and pathological characteristics, we consider that the use of PCBs for copy paper should be discontinued in any country in order to prevent another occurrence of "Yusho". The Japanese makers of the paper are said to have acted quickly along this line in April, 1971. To our regret, however, there have been no control measures set up by the government against the use of PCBs and a considerable amount of the PCB-polluted papers are still widely used in Japan.

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PCB and the Paper Industry—A Progress Report

by Paul E. Trout*

The paper industry's experiences with PCBs were chronologically reviewed at a recent "PCB Workshop" sponsored by the Grocery Manufacturers of America, Inc. (1). This history goes back somewhat over a year, at which time two paperboard manufacturers were apprised of the presence of PCBs in folding cartons for packaging dried fruit.

These two manufacturers immediately began searching for the source of the PCB contamination, screening all converting materials used in making cartons from the paperboard. These materials, including printing inks, varnishes and adhesives, proved not to be the source of the contamination. Examination of the fibrous materials used in the paperboard showed the source of PCB contamination to be some of the paperstocks used in manufacturing the paperboard. Certain high quality white and colored paperstock grades, such as ledger papers, were found to contain carbonless carbon papers which were the source of the PCBs.

PCBs at that time were used as one component of the dye carrier in the carbonless carbon paper system.

The American Paper Institute, the industry association, alerted the paper industry to this source of PCB contamination. Combination paperboard manufacturers, those who use recycled fibers in paperboard manufacture, immediately adopted operating procedures to eliminate the use of carbonless carbon papers and thus to minimize the PCBs in the paperboard.

This action unquestionably was essential. Yet, in one respect, it does run counter to the national interest and the goals of the solid waste program of the Environmental Protection Agency. The combination paperboard industry now uses 70% of all paper that is recycled in the United States. Additionally, the paper industry is being implored by government agencies to recycle more waste-paper in order to help combat our mounting solid waste problem.

Continuing research by the industry also showed that virgin fiber grades of paper and paperboard sometimes contained measurable amounts of PCBs, even though no carbonless carbon papers were used in their manufacture. Since PCBs have been established to be widespread in both our air and water environment (2, 3, 4, 5), the presence of PCBs in virgin fiber products is felt to be a reflection of these background environmental levels.

The Monsanto Company, sole domestic manufacturer of PCBs, withdrew PCBs from sale for other than closed system applications as of September 1, 1970. The manufacturers of carbonless carbon papers discontinued the use of PCBs in their product on June 1, 1971. These actions, together with the paper industry's elimination of carbonless carbon papers from paperboards used for food packaging, have resulted in marked reductions in the levels of PCBs in combination paperboard. They are also expected to show decreasing environmental or background PCB levels in the future.

Under the sponsorship of The American Paper Institute (A P I), research is currently in progress at Hazleton Laboratories, Inc. to study the mechanism by which PCBs migrate from paperboard to various food products and, also, to survey the levels of PCBs in United States pulps, papers and paperboards.

The former study is only well begun so I am

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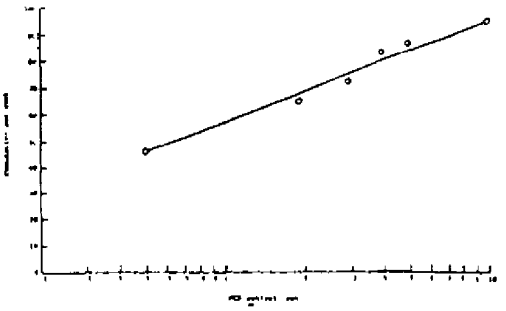

FIGURE 1 Cumulative-distribution of PCB in 676 samples of paper and paperboard

unable to present any meaningful data on migration to you at this time. The survey study is progressing smoothly, however, with approximately 676 samples having been analyzed to date. The results of these analyses are shown as a cumulative-distribution in Fig. 1. They have not yet been classified according to paper or paperboard type, so represent a broad spectrum of virgin and reclaimed paper and paperboard materials. This cumulative distribution shows 94% of all the samples to have PCB contents less than 10 ppm; 86% less than 5 ppm; and 46% less than 0.5 ppm (not detectable).

A second survey study is being sponsored by the Boxboard Research and Development Associ-

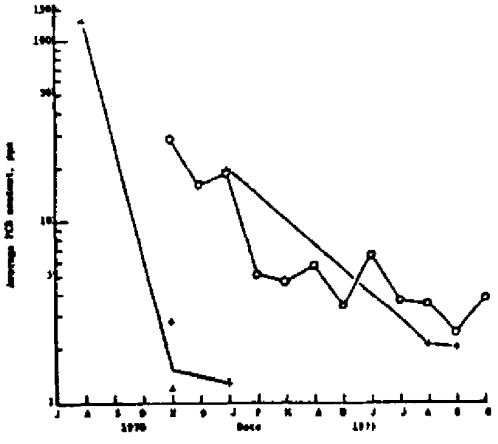

FIGURE 2 Effect of furnish control on PCB content of combination paperboard

Table 1. Estimated PCB content of typical packaged foods

Product	Product weight, oz	Carton product ratio	Calculated ppm PCB in food product for 33% transfer from cartons containing	
			5 ppm	10 ppm
Rice	42	0.048	0.08	0.16
	28	0.045	0.07	0.14
	14	0.053	0.09	0.17
Uncooked cereal	22	0.07	0.11	0.22
	11	0.096	0.16	0.32
Candy gum drops	6	0.08	0.13	0.26
Spaghetti	48	0.056	0.09	0.18
	16	0.06	0.10	0.20
	8	0.136	0.22	0.45
Raisins	15	0.052	0.09	0.17
	1.5	0.13	0.22	0.44

ation at The Institute of Paper Chemistry. This study is concerned only with recycled fiber paperboards. Preliminary data from this study indicate a mean PCB value of 3.6 ppm and an average PCB value of 6.4 ppm.

That the prompt action of the paper industry has indeed been effective in reducing PCB levels in food packaging materials can be seen from Fig. 2. Figure 2 depicts the change in PCB content with time for several grades of recycled fiber paperboard, where sufficient data were available to permit reconstruction of such a history. Similar histories could be developed for other food-packaging grades. This however would not add materially to our understanding of the problem more than is already seen from Fig. 2.

Although we do not yet have the results of the A.P.I. migration study, preliminary research by one A.P.I. member indicates that PCB migration from paperboard to high fat-content products does not exceed 33% of the total PCB in the paperboard, even in the absence of any protective barrier between the paperboard and the product. Based on this 33% migration factor and PCB levels of 5 to 10 ppm as being common in paper and paperboard, we can estimate expected levels of PCBs in products packaged directly therein

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such calculations are shown in Table 1 for typical foods now packaged in paperboard cartons Since, in most instances, the ratio of carton weight to product weight is normally of the order of 1 to 20, PCB levels in food products on the market today would be expected to be generally well below one-half ppm

This expectation is in reasonable agreement with the preliminary results of the Food and Drug Administration food survey presented by Dr. V. O Wodicka at the previously mentioned workshop [1] With one exception (0 6 ppm), the mean values of PCBs in fifteen food commodities ranged from 0 005 ppm to 0 1 ppm

These preliminary data indicate that PCB levels currently manufactured paper and paperboard food packaging materials are not such as to represent a hazard to public health These present levels are expected to decrease further as corrective actions, that have been taken by the industries involved, become fully effective

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Levels of Polychlorinated Biphenyls in Foods in Sweden

by Fredrik Berglund, M. D.*

PCBs have been used in industry in Sweden since 1929, initially only in electric transformers and capacitors, later also in paints, lacquers etc. The importation of PCBs to Sweden in 1970 was close to 500 tons. Approximately half of this amount was exported to other countries in electric capacitors. The use of PCBs in dyes was 65 tons in 1968 but was voluntarily diminished by industry to 35 tons in 1970. The Swedish Riksdag (parliament) has enacted the 1971 PCB Act, authorizing the government to prescribe conditions regarding importation, production, offering for sale and handling of PCBs, but detailed regulations have unfortunately not yet been published.

The high degree of persistence and lipid solubility of the PCBs have led to their accumulation in some foods of animal origin. In Sweden they now occur in the natural environment roughly in the same amounts as the chlorinated pesticides (1). The special hydrographical conditions of the Baltic favor the accumulation of PCBs in certain species and areas. The water exchange with the North Sea is very limited because of the thresholds (8 m and 18 m) and the narrowness of the Danish Sounds. The wide archipelagos at some places also make possible in some localities high concentrations of pollution, e.g., outside of Stockholm.

Table 1 briefly summarizes some of the earlier data, illustrating these points. The difference in levels of total DDT equivalents and PCBs between the Swedish west coast and the Baltic is more than 5-fold in fish oil and almost 10-fold in herring. The levels in fat are relatively high in all species shown. The role of the food chain is shown by the high levels in seal and by the extremely high levels in the white-tailed eagles from the Stockholm archipelago. Their muscle fat contained about 2.5% of total DDT metabolites and 1.4% of PCBs. The Stockholm archipelago is evidently heavily contaminated (cf below). The very high levels of DDT and of PCBs in muscle fat compared with the levels in eggs are most probably due to sampling from unrelated individuals. The muscle samples were from sick birds, whereas the eggs derived from apparently healthy birds.

There are only few data from seal. The levels of ΣDDT and of PCBs per kg fat show fair agreement between seal pup and seal milk (from the stomach of one of the pups).

The samples were analyzed by gas chromatography and electron capture detection, combined with treatments with sulphuric acid and potassium hydroxide. The principle PCB components were found to have 7–14 chlorine atoms, with an increase of those with higher chlorine content as the PCBs passed along the food chain.

Analyses of PCBs were later taken up by Westöö & Norén (2). After extraction and routine clean-up, the extracts were separated by thin-layer chromatography into two groups, one of which contained PCBs and p,p'-DDE, o,p'-DDT, o,p'-DDE. The PCBs were determined by gas chromatography of this group, before and after oxidation of the organochlorine pesticides. Some of the PCBs were analyzed by gas chromatography without decomposition of the organochlorine compounds. Recoveries averaged 96–101% for PCBs added to purified fish extracts before application to thin-layer plate (2).

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Table 1. Average levels of organochlorine compounds in some Swedish marine organisms 1965–1968 *Modified from (1).*

Species	Locality	Fat content	ΣDDT mg/kg fat	mg/kg	PCB mg/kg fat	mg/kg
Herring	W. coast		1 9		0 75	
	Baltic (18)	4 4%	17	68	6 6	27
Fish oil	W. coast	100%	2		7	
	Baltic	100%	18		3 5	
White tailed eagle						
muscle	Stockholm (4)	1 5%	25 000	330	14 000	190
eggs	Stockholm (5)	5 6%	1 000		540	
Seal	Gulf of Bothnia (2)	54%	120	63	13	6 8
Seal pup	Gulf of Finland (2)	60%	42	25	6 5	3 9
Seal milk	Gulf of Finland (1)	31%	36	11	4 5	1 4

Table 2. *Levels of DDT, DDE, DDD and PCBs in some fish in Sweden 1967–1969. Modified from (2).*

Fish	(n)	Range mg/kg	DDT n	DDE n	DDD n	PCB n
<4% fat freshwater	(87)	0–0 1	86	84	87	86
		0 1–1 0	1	3		1
<4% fat saltwater	(65)	0–0 1	57	59	63	58
		0 1–1 0	8	8		7
>4% fat saltwater	(34)	0–0 1	9	14	23	13
		0 1–1 0	24	20	11	19
		1 0–3.0	1			2

Table 3. Levels of organochlorine compounds in fish in Sweden 1967–1970. Modified from (3).

Species	Locality (No. of samples)	Fat content	ΣDDT mg/kg	PCBs mg/kg
Herring, *Clupea harengus*	Baltic (72)	3–20%	1 17± 061	0 49± 061
	S Baltic, deep-frozen (16)	3–20%	1 40± 079	0 27± 017
Eel, *Anguilla anguilla*	Baltic (43)	25%	0 50± 035	0 25± 030
	W. coast (11)		0 26± 050	0 43± 134
Cod, *Gadus morrhua*	Baltic (30)	<2%	0 05	0.02
			(0–0 2)	(0–0 1)
Cod liver	Baltic (7)	40–70%	10–22	2–5
	W. coast (3)		2–5	2–4
Salmon, *Salmo salar*	W. coast (5)	10–15%	0 06	Trace
			(01– 07)	
	Lakes (5)	10–15%	2 63± 72	0 58± 177
Pike, *Esox lucius*	Lakes (37)	<2%	0 06	<0 1
			(0–0 3)	(0–0 6)

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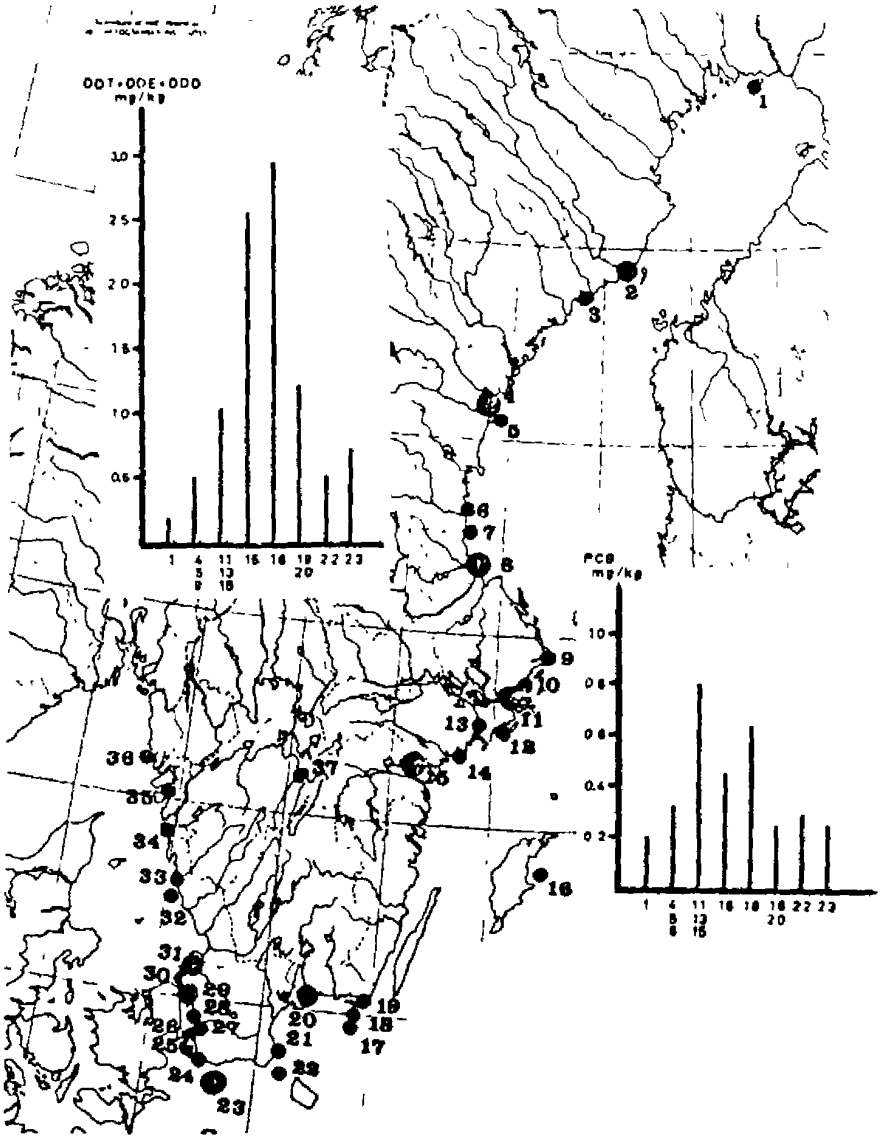

FIGURE 1 Average levels of organochlorine compounds in Baltic herring from different water areas Modified from (3)

The preliminary survey of organochlorine compounds and PCBs in less than 200 samples of fish is summarized in Table 2 Levels of DDT, DDEs or PCBs above 0 1 mg/kg were only rarely seen in lean fish, i.e in fish with less than 4% fat in their flesh, but occurred in more than half of the samples with more than 4% fat.

Westöö & Norén (3) later published analyses on about 1,000 samples of fish from lakes, rivers, the Baltic Sea and the Atlantic Ocean (Table 3).

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Table 4. Levels of DDT, DDE and PCBs in some foods in Sweden 1967–1969. Modified from (4)

Food	(n)	Range mg/kg	DDT n	DDE n	PCBs n
Margarine	(115)	0–0.1	115	115	115
Vegetable oils	(197)	0–0.1	190	197	197
		0.1–1.0	1		
Beef	(34)	0–0.1	34	34	34
Lamb fat	(10)	0–0.1	10	10	10
Pork	(107)	0–0.1	104	104	106
		0.1–1.0	6	3	1
Chicken	(93)	0–0.1	93	93	93
Hen	(50)	0–0.1	50	49	50
		0.1–0.3		1	
Egg white*	(28)	0–0.1	28	28	28
Egg yolk*	(185)	0–0.1	176	176	183
		0.1–1.0	8	8	2
		1.0–6.0	1	1	

* Six in each sample

The levels of ΣDDT and of PCBs depended on the fat content of the fish and on geographical location.

Regular salmon, *Salmo salar*, with 10–15% fat, had an average DDT level of 0.06 mg/kg on the west coast and 2.6 mg/kg in lakes, and of PCBs only traces on the west coast but 0.6 mg/kg in the lakes. Herring and eel, both with fairly high fat contents, had high levels. The highest PCB levels in fish were found in 2 small samples of herring from the Stockholm archipelago, 2.8 and 2.5 mg/kg, and in 4 yellow eels close to Gothenburg, 1.5 mg/kg. Five chars, *Salmo salvelinus*, in Lake Vattern had an average fat content of 7% and PCB level of 1.3 mg/kg (not included in Table 3).

Cod and pike, both with less than 2% fat, usually had very low DDT and PCB levels. Cod liver, on the other hand, with 40–70% fat, had high levels of DDT and PCBs. Because of its high levels of DDT, cod liver from the Baltic was declared unfit for human consumption by the Swedish health authorities this year (1971).

Some of the geographical variation of PCB and DDT levels in herring is shown in Fig. 1. PCB levels are highest outside of Stockholm, whereas DDT is higher off Gotland (16) and Blekinge (18–20). Other PCB-contaminated fish mentioned above were the eels caught off Gothenburg (2, 3) and the chars in Lake Vattern (17).

In other foods the levels of DDT, DDE and PCBs were much lower than in fish (4), as shown in Table 4. With few exceptions, all the samples of the foods listed contained less than 0.1 mg/kg of each compound. Egg yolk showed some DDT levels, but PCB levels in whole eggs would still not be expected to exceed 0.1 mg/kg.

Table 5 shows the results of analyses on cow's milk, butter, and human milk. Analyses on cow's milk showed DDT less than 0.1, DDE less than 0.3 and PCBs less than 0.5 mg/kg on a fat basis. Analyses on a much larger number of samples of butter revealed levels of DDT below 0.13, of DDE below 0.1 and of PCB below 0.1 mg/kg, also on a fat basis. The difference between cow's milk and butter in terms of DDE and PCBs is probably only a matter of sensitivity of the method—there is no reason to suspect losses of DDE and PCBs in the churning process.

In the analysis of human milk there was no need to look for "human butter", since the levels of DDT, DDE and PCBs were much higher than in cow's milk. The DDT levels in whole milk show fair agreement with those in the U.S. (5) and England (6). The PCB levels average 0.5 mg/kg fat or 16 μg/kg whole milk. This average would probably only represent the Stockholm area since all the samples originated from a "human milk donor center" in Stockholm.

Recently Westöö et al. (7) also discovered PCBs in some samples of cereal products. The origin was found to be the packaging material. On thin-layer chromatography and on gas chromatography, the PCBs behaved as PCBs of type Clophen A 60. In several samples of one kind of imported children's food, the PCB levels exceeded 1 mg/kg. In one sample of this product, which had been stored at room temperature for two years, the level of PCB had increased to 11 mg/kg. The sale of this children's food in Sweden was stopped in July, 1971.

The main intake of PCBs via the food in Sweden thus occurs by eating fish. The average consumption of fish in Sweden 1961–1969 was 17 kg/person/year—and of crustaceans and molluscs, about 1 kg/year. In terms of fish flesh Westin (8) calculated an intake for 1965 of 3.7 g per person and day. Of this, about 2 g represent

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Table 5 Levels of DDT, DDE and PCBs in butter, cow's milk and human milk in Sweden 1967-1969 Calculated from (4).

Food (n)	Fat	DDT	DDE	DDT+DDE	PCBs
Cow's milk (11)	~3%	<0.1 mg/kg fat	<0.3 mg/kg fat		<0.5 mg/kg fat
Butter (154)	>81%	<0.13 mg/kg fat	<0.1 mg/kg fat		<0.1 mg/kg fat
Human milk (22)	3.25 ±0.11%	1.24±0.07 mg/kg fat 40±3.0 µg/kg milk	2.08±0.13 mg/kg fat 67±6.0 µg/kg milk	3.32±0.19 mg/kg fat 100±8.8 µg/kg milk	0.50±0.039 mg/kg fat 16±2.5 µg/kg milk

freshwater fish, 1 g caviar, and 1 g shellfish and molluscs together. The average intake of PCBs therefore probably does not exceed 1 µg per day but may well exceed 10 µg/day in people eating herring from the Baltic 3 times a week.

A suckling baby ingests about 0.15 litre of mother's milk per kg body weight daily in the 2nd and 3rd months of life, with an average PCB level of 15 µg/kg milk. This corresponds to 2.4 µg kg body weight per day. Thus we have a situation similar to that with DDT with the suckling baby getting the highest exposure. Also, it is known from Japan that PCBs pass the placental barrier (9).

Conclusions Proper food processing should not produce PCB levels higher than 0.1 mg/kg food, except in fish with more than 2% fat in edible portions. Human milk has low levels of PCBs, but due to the high intake of milk, the suckling baby will experience the heaviest exposure.

To avoid further food contamination in the future, the use of PCBs should only be allowed in closed systems and under most careful supervision. Less dangerous substitutes should be looked for in industry.

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Occurrence of Polychlorinated Biphenyls in Humans*

by Harold A. Price and Robert L. Welch†

In 1967 the Human Monitoring Survey (1) was established by the Pesticides Program of the U.S. Department of Health, Education and Welfare (now, Division of Pesticide Community Studies, E.P.A.) to determine on a national scale the levels and trends of certain more commonly-used pesticide chemicals in the general population. Initially, this program was limited to the identification and measurement of chlorinated hydrocarbon residues in human adipose tissue and blood serum. The Michigan Department of Public Health has been one of several state health laboratories participating in the analysis of samples, collected by the State Services Branch of the Division of Pesticide Community Studies, from hospitals located in approximately 30 states. For the purpose of obtaining poolable data, the state laboratories use methodologies recommended by the Perrine Primate Laboratory, E.P.A. (Florida), which is responsible for methodology development, the operation of the quality control program, and serves as a repository of reference standards.

Since 1966 our laboratory has been conducting routine analysis of human adipose samples for organochlorine pesticide residues by gas chromatography, utilizing electron capture detection. In many instances, we observed numerous unidentified peaks recurring in a repeated pattern on chromatograms, some eluting much later than p,p'DDT. Our attention became focused on polychlorinated biphenyls (PCBs), after the Perrine Primate Laboratory alerted laboratories involved with the human monitoring program and community studies on pesticides of the possible interference of pesticide residue analysis by these compounds. This was prompted by early reports of research workers in Europe and the United States finding PCB residues in animal and environmental media (2, 3, 4). Early confirmation of some of these compounds had been obtained with a combined gas chromatograph-mass spectrometer from extracts of fish, sea birds, conifer needles, and some samples of human depot fat (5).

In March, 1969, one of Michigan's state laboratories found 19 ppm DDT in canned coho salmon during routine residue analysis. Our residue analysis on a similar sample seemed to corroborate this finding. However, considerable interference by "artifact" peaks was evident on the chromatogram, causing difficulty in both qualitative and quantitative analysis (2, 6) of pesticide residues. To a lesser extent, similar peaks had been observed with some human adipose samples. These unknown peaks were ascertained later as polychlorinated biphenyls when compared with several Monsanto Aroclors by electron capture gas chromatography and microcoulometry.

Prior to receipt of Monsanto Aroclors, we found a readily available source of a PCB indicator, e.g., residue analysis report forms. One of us had known by previous experience that carbonless copy paper has on one side a coating of microcapsules containing an Aroclor solution of a colorless dye (16). An extract of this paper pro-

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duced a chromatogram which matched a considerable portion of the interference observed with residues in coho salmon and human adipose tissue.

During the year following the coho salmon incident, our laboratory found substantial levels of polychlorinated biphenyls in several samples of human adipose tissue collected through the Human Monitoring Survey program. Three of these examples are given here to illustrate our findings.

Materials and Equipment

Materials and glassware used for extraction of samples and preparation cleanup of extracts are described fully elsewhere (7, 8).

A Micro-Tek Model 220 gas chromatograph (Tracor, Inc.) was used. It was equipped with two parallel-plate, tritium-source electron capture detectors, Vycor glass inserts installed at inlet ports to accommodate off-column injection, and U-shaped Pyrex glass columns (6 ft. × ¼ in. o.d.). Column packings (9) supplied by the Perrine Primate Laboratory consist of 1.5%OV-17/1.95%QF-1 (Column 1) and 4%SE-30/6%QF-1 (Column 2) on 80/100 mesh Chromosorb W HP. Operating temperatures of columns, detectors, and inlet were 200°C, 210°C, and 225°C, respectively. Carrier gas was nitrogen at flow rates of 65 ml/min through column 1 and 80 ml/min through column 2.

Reference standards of 1200 series Aroclors and organochlorine pesticides were obtained from the Pesticides Repository, Perrine Primate Laboratory, E.P.A., Perrine, Florida. Aroclors, products of Monsanto Company, are designated by numbers, such as 1260 which represents a mixture of chlorinated biphenyls having an average chlorine content of 60%.

For thin-layer chromatography, glass plates (Analtech, Inc.) precoated with aluminum oxide G, 250 microns thick, impregnated with 3.3% silver nitrate were used.

Method

The analytical scheme used for the preparation of these samples was the modified Mills procedure (8). One to three grams of tissue were extracted with hexane, partitioned with acetonitrile, and subjected to fractionation and cleanup by Florisil column chromatography. All of the PCB compounds were eluted in the first fraction (6% ethyl ether in petroleum ether), and this volume of eluate (200 ml) was reduced in a Kuderna Danish concentrator to 10 ml. A 5-µl aliquot was injected into the gas chromatograph. The extracts were diluted as required to obtain peaks within the linear range of the detector.

For certain selected samples, the polychlorinated biphenyls were separated from the organochlorine pesticide residues by application of the method of Armour and Burke (10). The 6% Florisil eluate was chromatographed on the silicic acid-Celite column with 250 ml of petroleum ether, which eluted the PCBs. The organochlorine pesticides were recovered next after elution with 200 ml of acetonitrile-hexane-methylene chloride (1.19:80).

Results and Discussion

In Fig. 1, electron capture chromatograms of human adipose tissue extract M69305 (6% Florisil eluate) and a standard solution of Aroclor 1260 are presented to illustrate that some of the "artifact" peaks in this tissue sample match those in the PCB standard. On the 4%SE-30/6%QF-1

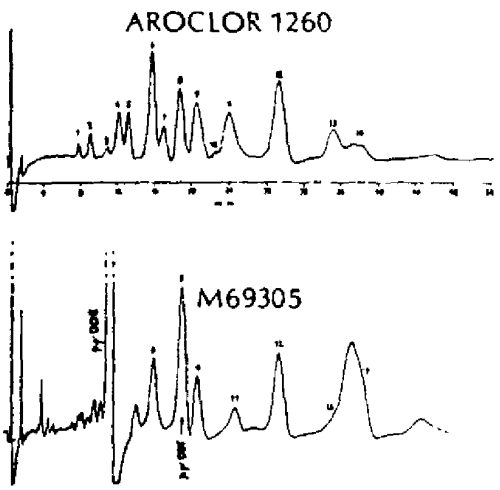

FIGURE 1. GLC-EC chromatogram of Aroclor 1260 (1.5 ng) and human adipose sample M69305. GLC conditions: 6'×¼" 4% SE-30/6% QF-1 column, oven temp 200°C, and nitrogen flow 75 ml/min.

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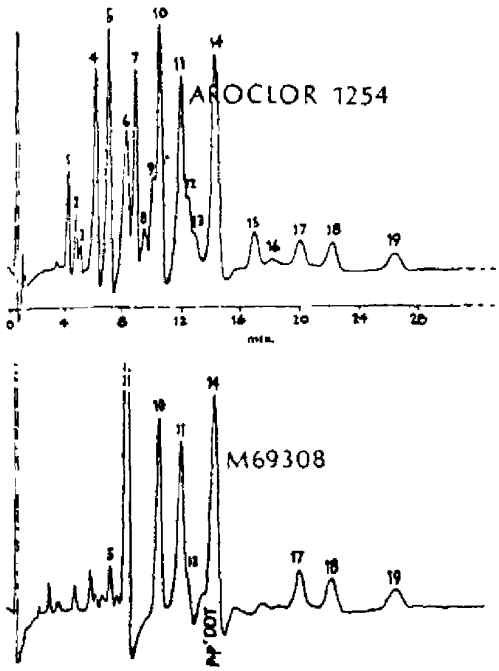

FIGURE 2. GLC-EC chromatogram of Aroclor 1254 (5.1 ng) and human adipose sample M69308. Peak 1' is 2,2',5,5'-tetrachlorobiphenyl, and peak 5 is 2,2',-4,5,5'-pentachlorobiphenyl. GLC conditions: 6'×¼" 4% SE-30/6% QF-1 column, oven temp 200°C, and nitrogen flow 75 ml/min.

column, p,p'DDT is completely masked by Peak 8 of Aroclor 1260; however, no interference is encountered with the quantitation of p,p'DDE.

On the basis of a major peak following p,p'DDT, the level of PCBs in this sample was estimated to be seven parts per million as Aroclor 1260. For estimating PCB levels by gas chromatography, we use Peak 12, preferably on 1.5%OV-17/1.95%QF-1 column, as a reference in Aroclor 1260 which has the following retention time relative to aldrin (R_t = 1.00):

Column	Aroclor Peak	p,p'DDE	p,p'DDT
OV-17/QF-1	6.4	2.23	4.18
SE-30/QF-1	4.83	1.82	3.12

In this sample, PCBs ranging from hexachlorobiphenyls to decachlorobiphenyl were confirmed by combined gas chromatography-mass spectrometry (11).

Fig. 2 shows that tissue extract M69308 contains some components which are present in Aroclor 1254. Approximately 20 ppm PCBs as Aroclor 1254 was determined by gas chromatography. Biros (11) confirmed the presence of pentachlorobiphenyls and hexachlorobiphenyls in addition to p,p'DDE. The largest unlabeled peak following Peak 5 in sample M69308 is p,p'DDE. The level of p,p'DDT in this sample was too low for confirmation by mass spectrometry, and its peak is masked by Peak 14 of Aroclor 1254 on the SE-30/QF-1 column used in this illustration.

In the spring of 1970, we found approximately 100 ppm PCBs in a sample of subcutaneous adipose tissue (M70227) which was obtained from a hospital in southeastern Michigan. The subject was a white male, age 77, whose demise followed a pulmonary thrombo embolism.

An electron capture chromatogram of the 6% Florisil column eluate of this sample is illustrated in Fig. 3 and is compared with a chromatogram of Aroclor 1260. This extract contains late eluting isomers that are also components of Aroclor

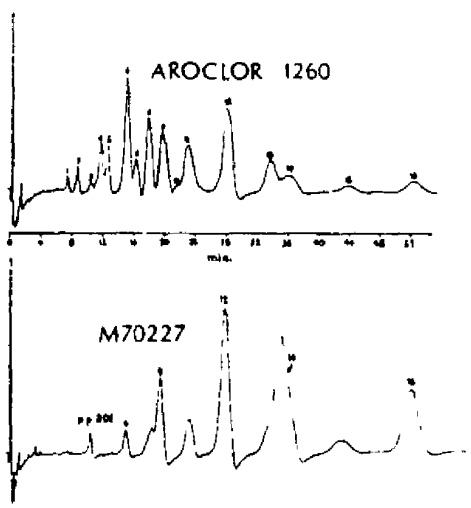

FIGURE 3. GLC-EC chromatogram of Aroclor 1260 (2.1 ng) and human adipose sample M70227 (30.5 mg, 6% Florisil fraction). GLC conditions: 6'×¼"% SE-30/6% QF-1 column, oven temp 200°C, and nitrogen flow 80 ml/min.

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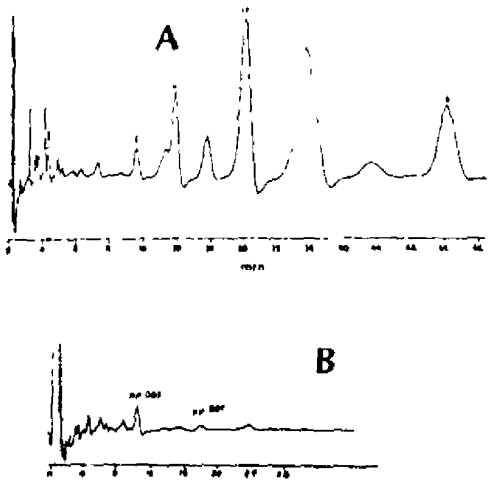

FIGURE 4 GLC-EC chromatogram showing separation of PCB (A) and organochlorine pesticides (B) by method of Armour and Burke GLC conditions same as Fig. 3. Weight of sample injected 30 5 μg.

1268, which makes matching to any particular Aroclor difficult. Fig 4 shows the separation of PCBs from organochlorine pesticides by the method of Armour and Burke (10), although some of the p,p'DDE eluted in Fraction A in this case. On the basis of a chromatogram of the second eluate from the silicic acid-Celite column resulting from a subsequent effort, residues of 0.37 ppm p,p'DDT and 0 81 ppm p,p'DDE were found in the fat of this sample. Using the combined gas chromatograph-mass spectrometer, Biros (12) confirmed the presence of p,p'DDE in M70227 as well as ten polychlorinated biphenyls ranging, from hexachloro- to nonachloro-compounds. These compounds are found in Aroclors 1260, 1262, and 1268.

Further examination of other tissues of the same autopsy case revealed a good correlation of PCB levels when compared on the basis of extractable lipids as demonstrated in Table 1. These data are good estimates calculated from the height of a peak corresponding to Peak 12 of Aroclor 1260 on the OV-17/QF-1 column. PCB peaks in M70227 appear to be a complex mixture of several Aroclors not usually observed in human adipose tissue.

Efforts to determine the source of PCBs in sample M70227 have not been successful Indications are that this individual was exposed to PCBs during his lifetime As PCBs enter a biological system, the less chlorinated isomers are either metabolized or excreted, which changes the composition of original Aroclors, so that chromatograms of these mixtures from biological samples do not match exactly those of reference standards This has also been observed with PCBs in M70227 In fact, more than 4,000 human adipose samples examined in our laboratory have produced chromatograms that do not exactly match those of standard Aroclor solutions We have found the distribution of PCBs in samples, such as M70227, to be uniform throughout the sample as received, indicating that these samples have not been contaminated by PCBs during handling As for all samples, M70227 was collected from an autopsy examination through the cooperation of pathologists, according to directions specified by the State Services Branch of the Division of Pesticide Community Studies, E P A

As many investigators of PCBs have found, one of the principal sources of polychlorinated biphenyls in the biological system is the food chain (5, 13, 14). Coho salmon, for example had been a source of PCBs in food until it exceeded the action level of 5 ppm.

Another possible avenue of human exposure to polychlorinated biphenyls may be indicated by their presence in some house dust (vacuum sweepings). Our examination of house dust from residences of occupationally-exposed population of southwestern Michigan revealed that several samples contained up to 180 ppm PCBs, mainly Aroclor 1254.

Table 1. Levels of PCB's in Various Tissues Related to Sample M70227*

Tissue	% Lipid ext'd	PCB level, ppm	
		Wet weight basis	Fat basis
S Adipose*	41 1	75	180
S. Adipose	63 9	100	155
S. Adipose	32 8	50	150
P. Adipose	44 1	50	115
Liver	0 08	2	250
Kidney	0 06	0 75	125

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Table 2. Distribution of PCB Levels in Adipose Tissue of the General Population—Analysis by Gas Chromatography

Level, ppm	Samples	Percent of total
Negative	4	2.0
Trace to <1.0	109	55.0
1.0–2.0	72	36.7
>2.0	11	5.6

As mentioned previously, levels of polychlorinated biphenyls in human tissue extracts illustrated in Figs. 1, 2, and 3 were determined by electron capture gas chromatography using a major peak after p,pDDT (Peak 12) as a reference peak for Aroclor 1260. Since April, 1971, our laboratory has run semiquantitative analysis of polychlorinated biphenyls in samples of human adipose tissue by both electron capture gas chromatography and thin-layer chromatography. The latter based on total chlorine is an adaptation of a procedure reported by Mulhern et al., (7, 15). After gas chromatographic analysis is completed, the remaining extract is evaporated, and pesticide residues are dehydrochlorinated with ethanolic potassium hydroxide and oxidized with chromic oxide. The concentrated extract of PCBs remaining is spotted on a thin-layer plate, and the developed spots after exposure to ultraviolet light are compared with several spots of standard Aroclor 1260 at different concentrations. The limit of detection is 250 ng of Aroclor 1260. Results in Tables 2 and 3 indicate that both methods provide similar information, but thin-layer chromatography is preferred. On the basis of samples received and analyzed by our laboratory, these data show the distribution of PCB levels in adipose tissue of the general population.

Table 3. Distribution of PCB Levels in Adipose Tissue of the General Population—Analysis by Thin-Layer Chromatography

Level, ppm	Samples	Percent of total
Negative	20	10.3
Trace to <1.0	87	44.8
1.0–2.0	70	36.1
>2.0	17	8.8

Summary

According to samples of human adipose tissue received by our laboratory, 41–45% of the general population have levels of 1.0 ppm or more (wet weight) polychlorinated biphenyls with isomers from Aroclors 1254, 1260, 1262, and 1268. The presence of PCBs ranging from pentachlorobiphenyls to decachlorobiphenyl has been confirmed in selected samples, M69305, M69308, and M170227, by the use of combined gas chromatography-mass spectrometry.

Acknowledgements

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Levels of Polychlorinated Biphenyls in Adipose Tissue of the General Population of the Nation

by Anne R. Yobs, M.D.*

Polychlorinated biphenyls (PCBs) have been reported in many different parts of the environment in this country (1-3). The purpose of this report is to present preliminary results from a monitoring program in which these materials are routinely sought and quantitated.

The Human Monitoring Survey, established in 1967 by the Pesticides Program, DHEW (now Division of Pesticide Community Studies, EPA), determines, on a continuing basis, the exposure to pesticides experienced by the general population by measuring levels of pesticide residues present in tissues or excreted in urine. Initially, technological limitations and resource restrictions limited the Survey to the identification and measurement of those chlorinated hydrocarbon residues which are stored in mensurable amounts in mammalian adipose tissue, or which can be measured in blood, these residues being a reflection of past exposure. The initial program plan has been and continues to be reviewed frequently with reference to technological and/or research developments to identify other groups of pesticides and other materials of interest, which can be incorporated with slight modification of the existing program.

Samples are collected through the direct cooperation of pathologists, who are in hospital or private practice or who are in public service as city or county medical examiners. Samples are collected from both sexes in all age and racial groups. Adipose samples are collected from tissues removed for therapeutic surgery or from postmortem examinations, the latter including people who have died accidentally (trauma) or during relatively brief hospitalization. No samples are accepted from institutions for long-term care of the chronically ill patient.

All samples are analyzed by laboratories established under contract with State Health Departments or at community study projects in Michigan, Florida and Colorado. These laboratories use analytical methodologies specified by the program on the advice of technical consultants and are required to maintain acceptable levels of performance, as demonstrated in both inter- and intra-laboratory quality control programs. Technical consultation for analytical aspects of the Survey is provided by the Chemistry Branch, Perrine Primate Laboratory, EPA, under the direction of Henry F. Enos, Ph.D., Chief.

In 1969, with the increased interest in polychlorinated biphenyls, it was recognized that PCBs probably occur in several segments of the environment and that their presence would distort analytical values for certain pesticides, especially selected DDT residues. The monitoring laboratories were therefore asked to report all samples suspected of containing PCBs by gas-liquid chromatography. A reporting system was developed based on rough quantitation, as follows: negative, present in usual amounts, present in greater or lesser amounts than usual. Samples collected in late 1968 and 1969 showed that PCBs were indeed present in a significant portion

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of the general population of the country over a wide geographic distribution. Positive samples were reported from 14 States, including Michigan, New York, Minnesota, California, Massachusetts, Georgia, Kentucky, Illinois, North Carolina, South Dakota, Ohio, Louisiana, Delaware and Arkansas. To insure that proper identification was being made, two samples with higher levels were confirmed by combined gas liquid chromatography-mass spectroscopy (4). These two cases are discussed in another paper in this symposium (5).

Based on these preliminary findings and certain as yet unpublished information about the effect of PCBs on the accuracy of measurement of residues of DDT (Enos, H. F., personal communication), high priority was given by the Perrine Laboratory to the development and evaluation of an analytical method which would separate PCBs from pesticides permitting accurate quantitation of pesticides and confirmation of PCB levels. The resulting methodology is a further modification of the Mills-Olney-Gaither procedure in which adipose tissue is subjected to extraction by petroleum ether, acetonitrile partitioning, and Florisil cleanup. A portion of the resulting 6% ethyl ether/petroleum ether eluate, in concentrate form, is treated with KOH to effectuate dehydrochlorination of DDT and DDD to their olefins, thus eliminating the problem of separating these pesticides from the PCBs. Oxidative treatment is then applied to convert any interfering DDE to p,p'-dichlorobenzophenone which has an Rf value different from the PCBs. The PCBs are then determined by thin layer chromatography (6).

On April 15, 1971, all monitoring laboratories in the Human Monitoring Survey adopted this methodology for the analysis of all adipose samples with the lowest limit of sensitivity being 1.0 ppm. Aliquots of all samples in which measurable amounts of PCBs are found are saved for future confirmation by mass spectroscopy.

Table 1. Incidence of polychlorinated biphenyls in adipose of the general population of the nation.

	Reported		Analyzed	
	No.	%	No.	%
Total	637	100.0	688	100.0
Negative	314	49.3	235	34.2
Trace–<1.0 ppm	125	19.6	229	33.3
1–2 ppm	165	25.9	188	27.3
>2 ppm	33	5.2	36	5.2

Table 2. Descriptive statistics of samples analyzed

		Negative and trace <1.0 ppm		>1.0 ppm	
		No.	%	No.	%
Total number		439	100.0	198	100.0
Sex					
Male		221	50.3	127	64.1
Female		218	49.7	71	35.9
Race					
White		381	86.8	151	76.3
Nonwhite		58	13.2	47	23.7
Samples from					
Therapeutic surgery		95	21.6	29	14.6
Postmortem		344	78.4	169	85.4
Diagnostic group					
Neoplasms	140–209	77	17.5	39	19.7
Circulatory system	390–459	121	27.6	61	30.8
Gastrointestinal system	530–565	44	10.0	16	8.1
Liver & gall bladder	570–575	20	4.6	6	3.0
Pancreas	577	0	0.0	2	1.0
Urinary system	580–595	11	2.5	7	3.5
Congenital Anomalies	740–759	5	1.1	1	0.5
Accidents & violence	E numbers	16	3.6	7	3.5
All other		145	33.0	59	29.8
		439	99.0	198	99.9

Results and Discussion

Analytical results for 637 samples have been reported and are summarized in Table 1 (additional samples have been analyzed but have not as yet been reported). Of the 637 samples reported, 198 (31.1%) contained measurable amounts of PCBs and 125 (19.6%) contained trace amounts, with the balance being negative. These samples were collected from 40 pathology in 38 cities distributed over 18 States and the District of Columbia. The States are Arkansas, Illinois, Louisiana, Oklahoma, South Da-

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Tennessee, Oregon, Pennsylvania, Florida, Kansas, Maine, Georgia, North Carolina, California, Michigan, New York, Ohio and Kentucky. Positive samples came from every hospital, city and state sampled. It, therefore, appears that these materials are widely found in the population. Details of distribution by sex and race, collection procedure, and diagnostic groups are summarized in Table 2. The difference between figures for the positive and negative groups does not appear to be significant, although no statistical evaluation has been attempted because of the preliminary nature of this report. Since a statistical design has been established and is being followed for sample collection for the Human Monitoring Survey, in due time valid statistical analysis will be possible and will then be performed.

Summary

Polychlorinated biphenyls have been found in measurable amounts in 31.1% of 637 samples of human adipose tissue collected from the general population as a part of the Human Monitoring Survey. Sample collection involved 18 States and the District of Columbia. Positive samples were obtained from every state sampled.

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