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PCB AND OTHER INDUSTRIAL HALOGENATED HYDROCARBONS IN THE ENVIRONMENT

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ABSTRACT - Industrial applications of polychlorinated biphenyls (PCB), chlorinated naphthalenes, chlorinated paraffins, chlorinated benzenes, polybrominated biphenyls, chloro-bromo biphenyls, chloro-hydroxy biphenyls, and halogenated carboxylic acids are described. A list of other halogenated hydrocarbons and derivatives, used as solvents, fumigants, refrigerants, flame retardants, aerosol propellants, heat-transfer media, hydraulic fluids, etc., is included. Current methods for the measurement of PCB are reviewed. PCB and p,p'-DDE levels in fishes and aquatic birds, reported in the literature, are summarized. Recently determined PCB concentrations in Atlantic salmon, bluefin, yellowfin, and skipjack tuna, bluefish, swordfish, and blue marlin, cod, white hake, plaice, and redfish, double-crested cormorant, herring gull, black duck, and guillemot are presented. The determination of polychlorinated terphenyls (PCT) in biological samples and the behaviour of polybrominated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans during cleanup and gas chromatography is described. Biological effects of PCB and other halogenated hydrocarbons are reviewed. The sources of PCB leakage into the environment and their circulation are discussed. Analytical procedure for the determination of PCB and organochlorine pesticides based on the modified cleanup chromatography of Holden and Marsden is described.

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INTRODUCTION

The persistence of chlorinated hydrocarbon pesticides in the environment and their accumulation in the food chains is well known. A variety of halogenated hydrocarbons is used in industry and, as demonstrated in the case of PCB, the environmental behaviour of these compounds may be similar to that of chlorinated hydrocarbon pesticides.

Several PCB review papers appeared recently in the literature (Risebrough et al., 1968, Risebrough, 1969, Veith et al., 1970, Gustafson, 1970, Peakall et al., 1970, and Reynolds, 1971). Interest in environmental aspects of PCB is growing fast and much new information became available. In the following, only articles not cited in the above reviews will be mentioned. Other halogenated hydrocarbons of industrial importance are also included in the literature survey.

Uses of PCB and other halogenated hydrocarbons

No data on the production or consumption of PCB in the world are available except for Finland where according to unofficial commercial statistics, the annual consumption of PCB is about 250 metric tons (Helminen, 1970).

PCB containing 20-50% chlorine increase the oxidation stability and eliminate flammability of mixtures of mineral and silicone oils (Marek et al., 1968). A trichlorobiphenyl preparation (Pyranol 1499) may be used to prepare media with high dielectric strength (Cox, 1970). PCB are one of the ingredients for coloring of molten linear polyesters (Brinkman, Jr., 1969). Details of the industrial preparation of PCB in the U.S.S.R. were published (Trofimov et al., 1969). The crude chlorinated product contains 1-2.5% hydrochloric acid and traces of ferric chloride. The latter forms complex compounds diminishing the insulating properties of the preparation. The impurities can be removed by treatment of crude PCB with sodium hydroxide at 150-170°C and distillation. This is very likely the process generating highly toxic chlorinated dibenzofurans found in some PCB preparations (Vos et al., 1970b). The preparation of 3,3',5,5'-tetrachloro-2,2',4,4',6,6'-hexafluorobiphenyl was described (Ishikawa, 1969) and polymethylated pentafluorobiphenyls were prepared (Brown et al., 1969). The use of mixed chloro-fluorobiphenyls in hydraulic fluids with improved heat stability, fire resistance, lubricity, viscosity, and anti-corrosive properties was patented (Boschan et al., 1970). Another patent describes the preparation of diamino-polyhalobiphenyls (halogen: chlorine, bromine) to be used as starting materials for the preparation of flame-resistant polymers and hardening agents for epoxy resins (Sobel et al., 1970). A new series of unsaturated, flame-resistant polyester resins, based on diols derived from decachlorobiphenyl was developed (Anon, 1971). The preparation of bis(chloromethyl)-octachlorobiphenyls as intermediates for manufacturing dyes, plastics,

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or plant protective agents was patented (Woppert et al., 1970). The flame retardant additive, Firemaster BP6 is hexabromobiphenyl (Michigan Chemical Corp., 1971). PCB may be used for quenching of heated metals (Massey, 1971). Aroclor 1221 was used in preparations increasing opacity and brilliance of fibrous and paper substrates (Vassiliades et al., 1971). Chlorinated biphenyls and trichlorobenzene are the insulating liquid in General Electric Pyranol transformers, induction voltage regulators and exciting-current interrupter switches. The first transformer Pyranol was introduced in 1932. It was later modified by the addition of tetraphenyl tin, used as hydrochloric acid scavenger. The present-day formulations contain diepoxide which has several advantages over tetraphenyl tin (General Electric, 1967). Trichlorobenzene is sometimes added to PCB preparations to lower the solidification temperature (Gambaro et al., 1969). A typical preparation contains 40% of trichlorobenzene and 60% of hexachlorobiphenyls (Jay, 1970). The impregnation of polypropylene with 5-20% trichlorobiphenyl and 0.1-10% epoxide stabilizer to produce dielectric films on capacitors was patented (Eustance, 1971). Traffic markings may contain PCB (Japan Paint Co., 1970). The preparation of isomer-free p,p'-disubstituted biphenyls from substituted phenylmercuric acetates was patented (Kraus et al., 1970).

Polymeric products of unknown composition, possibly incorporating oxygen, are formed from PCB on heating. The addition of organic phosphites such as diisopropylphosphite, and nitrogen or carbon dioxide atmosphere were used to suppress this reaction (Sullivan, 1971). The synthesis of some nitrobromobiphenyls was described (Dell'Erba et al., 1971), and the preparation of 3,5,3',5'-tetrabromo-2,4,2',4'-tetrahydroxybiphenyl, Tebrophen was patented (Pershin et al., 1971. This compound is an antiviral agent, effective particularly in viral eye infections (Nikolaeva et al., 1970). Routes for the synthesis of individual chlorobiphenyls with 4 and less and with more than 4 chlorine atoms, with special attention to the preparation of radioactively labelled chlorobiphenyls were discussed (Melvas, 1970; Wachtmeister et al., 1970). The preparation of

^{36}Cl-labelled PCB of the Aroclor 1248 and 1254 type for tracer studies was recently described (Stalling et al., 1971). More than 20 chlorobiphenyls were recently prepared (Hutzinger et al., 1971). Disposal techniques for PCB-containing wastes were discussed. PCB can be destroyed by incineration at temperatures above 800°C (Peterson, 1970).

Chlorinated 3-pentadecenyl phenyl methyl ether can be used as plasticizer and extender for polyvinylchloride (Ghatge et al., 1970).

Chlorinated naphthalenes are another group of industrially important chlorinated hydrocarbons. In the U.S.A., they are manufactured under the tradename Halowax (Anon.). Halowax 1000 is a mixture of mono- and dichloronaphthalenes

containing 26% chlorine and is used mainly in motor tune-up compounds and upper cylinder lubricants. Halowax 1031, mostly 1-chloronaphthalene is of better purity and has similar uses. Halowax 1001 and 1099 are mixtures of tri- and tetrachloronaphthalenes with a chlorine content of 50-52%, and are used as dielectrics, binders for electrical grade ceramics and paper coatings. Halowax 1013 and 1014 contain from 4 to 6 chlorine atoms per molecule (56-62% chlorine) and are used as insulators, oil additives, and flame retardants. Halowax 1051, basically octachloronaphthalene (70% chlorine) may be used as a component of organic fillers where flame retardancy is required.

A chlorinated hydrocarbon preparation, Cereclor 552 (mol. wt. 400, 52% chlorine) was used to flameproof polyacrylonitrile fibers (Torrance et al., 1971).

Chlorinated paraffins with 15 carbon atoms in the molecule, containing 50% chlorine were used to prepare dispersion-stable polyvinylchloride latexes (Iida et al., 1971). Chlorinated paraffins are also used in paper-sizing agents (Chiba et al., 1970), and probably the main application of these compounds is in the flameproofing of materials. Chlorinated paraffins used for this purpose contain 40-50% chlorine and 20-24 carbon atoms in the molecule (Anon., 1969). Chlorinated paraffins were used in flame retardant thermoplastic ethylene-vinyl acetate copolymer compositions (Kosaka et al., 1970). Chlorinated paraffins together with zinc fluoroborate and a nonionic emulsifier were used to improve the fire resistance of acrylic textiles (Fidell, 1971).

Flame retardant compounds may also be chemically incorporated into polymers. Such compounds contain, in addition to halogen atoms, one or two functional groups which can participate in the polycondensation reactions. Presently used compounds include chlorendic anhydride [1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-5-heptene-2,3-dicarboxylic anhydride], tetrachlorophthalic anhydride, tetrabromophthalic anhydride (Firemaster PHT4), and dimethyl-di-(3,5-dibromo-4-hydroxyphenyl)-methane (Firemaster BP4A, Michigan Chemical Corp.). Other compounds suggested for this purpose are 3,3',5,5'-tetrafluorobiphenyl-4,4'-dicarboxylic acid, 2,2',4,4'-tetrafluorobiphenyl-3,3'-dicarboxylic acid, 2,2',4,4'-tetrafluorobiphenyl-5,5'-dicarboxylic acid, 2,2',6,6'-tetrafluorobiphenyl-3,3'-dicarboxylic acid, 2,2',4,4',6,6'-hexafluorobiphenyl-3,3'-dicarboxylic acid, and 2,2',5,5'-tetrafluorobiphenyl-6,6'-dicarboxylic acid (Sugawara et al., 1971). Fumarate and maleate polyesters of 2,2',3,3',5,5',6,6'-octachloro-4,4'-(2-hydroxyethylene)-diaminobiphenyl and 2,2',3,3',5,5',6,6'-octachloro-4,4'-bis(diethylenedioxy)-biphenyl have excellent flame resistance (Vogt et al., 1971).

Chlorinated fatty acid esters are used as low-cost plasticizers for a variety of resins and plastic materials. Methyl dichlorostearate and Plasticizer MSP-500 (Anon., 1969) are

examples of this class of compounds.

As a rule, brominated compounds are about twice as effective fire retardants as chlorinated compounds. Aliphatic bromine compounds are about 1.5 times more effective than aromatic bromine compounds (Schneider et al., 1969).

Brominated vegetable oils are used as haze stabilizers in citrus-based soft drinks.

Chlorinated polymers such as chlorinated polyisoprene, polyethylene, and polypropylene, with a chlorine content of 40-68% are used as binders for paints and combination resins for printing inks (Hoehne et al., 1970). Halogenation of polyesters for the preparation of self-extinguishing films was patented. Such preparations contained 6-25% bromine and 3-6% chlorine (Jackson et al., 1971). Perfluorinated hydrocarbons have low boiling points for their molecular weight, extremely low surface tension, and very high density and viscosity. They are poor solvents for most compounds except gases. Perfluorinated hydrocarbons have an excellent chemical and thermal stability and very low toxicity (Sargent et al., 1970). Methylene chloride (10-80%) and perchloroethylene (0-20%) are used in heavy duty diphase cleaners and a method for their determination by gas chromatography was published (Bennett et al., 1971). Tri- and tetrachloroethylene mixed with surfactants to form water-in-oil type of emulsions can be used for cleaning ceramic, metals, and other materials (Johnson, 1971).

Other halogenated hydrocarbons are used as solvents, fumigants, refrigerants, aerosol propellants, etc. A list of the more important industrial halogenated hydrocarbons is included in Appendix.

Contamination of the environment by industrial halogenated hydrocarbons

PCB are used in a wide variety of products and hence may enter the environment via different routes. Direct spills or leakages from heat exchange systems are one such route and occurred for example in Escambia Bay, Florida (Duke et al., 1970). General aerial fallout may be another route since particularly the lower chlorinated biphenyls are appreciably volatile.

Sewage outfalls and ocean-dumped sludge are probably major sources of PCB. Concentration of PCB in raw sewage from the Glasgow area ranged from 0.1 to 14 ppm as Aroclor 1254 on wet weight basis, and it was estimated that the PCB discharge into the Clyde estuary is of the order of 1 ton per year. Similar estimates were obtained for the Manchester area and the Thames estuary (Holden, 1970a). In California, sewage outfalls discharge from 0.06 to 0.7 tons of PCB per year in water and

from 0.6 to 36 tons per year in sludge (Schmidt et al., 1971). Low molecular weight chlorinated paraffins and olefins, such as 1,2-dichloroethane, 1,1,2-trichloroethane, symmetrical and unsymmetrical tetrachloroethane, pentachloroethane, chlorinated butanes, cis- and trans-isomers of chlorinated 1-, and 2-butenes are byproducts of vinylchloride production by the oxychlorination process. Large quantities of these compounds are dumped into the sea and the hydrocarbons were recently detected in fish and water samples from the Norwegian, Barents, and North Sea (Jensen et al., 1970).

Only limited data on the occurrence of other halogenated hydrocarbons in the environment are available. A variety of halogenated hydrocarbons is released into the atmosphere, from where it may reach the aquatic environment. For example, about 3.6×10^5 t/year of tetrachloroethylene evaporates from dry cleaning solvents in the U.S.A. (Goldberg, 1970). Fluorodichloromethane, difluorodichloroethene, fluorotrichloromethane, difluorochloromethane, difluorodichloromethane, trifluorotrichloroethane, methylchloroform, vinylidene chloride, trichloroethylene, tetrachloroethylene, chlorobenzene, and dichlorobenzene were detected in the atmosphere of the U.S.S. Hammerhead (Saafeld, 1971), which may serve as a model of the earth's atmosphere. Some decomposition products of the above-mentioned hydrocarbons may also exist in the atmosphere. Thus the very toxic dichloroacetylene is generated by alkali from 1,1,2-trichloroethane (Saafeld, 1971).

Hexachlorobutadiene (132 mg/l), tetrachloroethylene (154 mg/l), trichloroethylene (65 mg/l), and carbon tetrachloride (29 mg/l) were detected by gas chromatography (5% tricresylphosphate on a diatomite at 130°C) in waste water from the production of hexachlorobutadiene (Mikhailok et al., 1970). An industrial mixture containing hexachlorocyclopentadiene was analysed by gas chromatography on silicone E-301 liquid phase at 160°C. Octachloropentadiene, hexachlorobenzene and unidentified impurities were also detected (Dzhioeva et al., 1970).

A maximum allowable concentration of 0.31 mg/l was recommended for allyl chloride in reservoir water (Karmazin, 1966). The suggested maximum allowable concentration of tetrachlorobenzene is 0.02 mg/l (Fomenko, 1965), and that of trichlorofluoropropane is 0.1 mg/l (Selyuzhitskii, 1963).

Suggested maximum permissible concentration of carbon tetrachloride in water reservoirs is 0.3 mg/l (Kutepov, 1968).

From 18 to 42 µg/l of organically bound chlorine was detected in Rhine water, 45 µg/l in waste water and 25 µg/l in biologically purified waste water. Most of the organochlorine compounds were adsorbed on suspended matter. The average 1969 content of these compounds in suspended matter, collected from the River Rhine at Düsseldorf was 66 mg/kg on dry weight basis (Koppe et al., 1970b).

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Analytical methods for PCB, chlorinated naphthalenes, and polychlorinated terphenyls, and other halogenated hydrocarbons

PCB accompany chlorinated hydrocarbon pesticides in the usual extraction and cleanup techniques and both groups must be separated before quantitation by gas chromatography. Column and thin-layer chromatography are usually used for the separation. PCB were eluted from Florisil columns with hexane; DDT and other pesticides with mixtures of ether and hexane (Reynolds, 1969). Another laboratory had difficulties with this technique and reported that DDT was already partly eluted with hexane (Bevenue et al., 1970). Column chromatography on silicic acid separates PCB from all common chlorinated hydrocarbon pesticides except p,p'-DDE (Holden et al., 1969), and under very carefully controlled conditions even from p,p'-DDE (Armour et al., 1970). Some carry-over of PCB into the pesticide fraction was demonstrated by a combined GLC-MS procedure when extracts containing more than 0.4 g fat were placed on the silicic acid column (Bellman et al., 1971). Small amounts of aromatic hydrocarbons such as benzene, present in some pesticide-grade hexanes affect significantly the elution patterns of PCB and organochlorine pesticides from silicic acid columns, and may be responsible for the discrepancies reported above (Zitko, 1971a).

Thin-layer chromatography on alumina with n-heptane as the developing solvent was used to separate PCB from organochlorine pesticides. Areas on the plates, containing the respective compounds were extracted with methanol-hexane and the extracts were analysed by gas chromatography (Westöö et al., 1970c). TLC on alumina, coated with silver nitrate, was used to semi-quantitatively determine PCB after oxidation of p,p'-DDE to 4,4'-dichlorobenzophenone with chromic oxide in acetic acid. Developing solvent was 5% benzene in hexane and the commercial PCB preparations Aroclor 1242, 1248, 1254, 1260, and 1262 moved as single spots with R_f 0.91-0.94 (Mulhern et al., 1971). A TLC technique based on two-dimensional development with n-heptane and n-heptane-acetone 98:2, respectively, was described (Febringer et al., 1971). PCB components can be effectively separated by reversed-phase TLC using liquid-paraffin impregnated silicic acid as the adsorbent and a mixture of acetonitrile, acetone, methanol, and water, 40:18:40:2, as the solvent (De Vos et al., 1971).

A method based on reversed liquid-liquid partition between water and Chromosorb W, coated with n-undecane and Carbowax 4000 was developed for the determination of PCB in water. The sensitivity of the method is in the ppt range (Ahling et al., 1970).

Gas chromatography of chlorinated biphenyls on capillary columns coated with polypropylene glycol 750 was described (Weingarten et al., 1962), and an excellent separation of mono-, di-, and trichlorobiphenyls by gas chromatography on polyphenyl

thioethers was patented (Emery et al., 1970). Various other phases are used for gas chromatography of PCB. One of the most frequently encountered is the silicone grease SE-30, often mixed with other materials such as QF-1.

Electron-capture detector response to mono- and dichlorobiphenyl was reported (Gregory, 1968). The response to mono-, di-, tri-, tetra-, penta-, hexa-, and octachlorobiphenyls, and to decachlorobiphenyl was recently determined (Zitko et al., 1971a). The detector response strongly increases with increasing number of chlorine atoms in the molecule. For example, the response of decachlorobiphenyl is 500 times stronger than the response of 4-chlorobiphenyl. Most of the increase occurs in the mono- to trichlorobiphenyl range and the response increases only by a factor of 2-3 between tetra- and decachlorobiphenyl. The detector response depends also on the chlorine substitution patterns. Thus chlorine substitution in positions 2 and 6 decreases, and vicinal substitution, particularly in positions 3 and 4 increases the electron-capture detector response. PCB found in wildlife are of the Aroclor 1254 or 1260 type; according to mass spectra, their components are tetra-, penta-, hexa-, and heptachlorobiphenyls (Koeman et al., 1970), and the detector response to these compounds is not likely to vary more than by a factor of 2, which is a reasonably good basis for quantification, even without detailed identification of the individual chlorinated biphenyls.

Carbon skeleton chromatography of Aroclor 1260 was recently described (Asai et al., 1971). The preparation is converted essentially into a mixture of cyclohexylbenzene and biphenyl at the catalyst temperature of 300°, and into cyclohexylbenzene and bicyclohexyl at 260°. The technique may be useful for confirmation purposes.

Computer-controlled gas chromatography-mass spectrometry was used to identify tetrachlorobiphenyls in a Los Angeles sewer extract and in a sturgeon ovary extract (Bonelli, 1971).

Randomization of chlorine atoms between phenyl groups occurs in the electron impact-induced fragmentation of PCB and with only one exception (2,2'-dichlorobiphenyl) the primary ion spectra of different isomers are virtually indistinguishable which means that the use of mass spectrometry for structural studies of PCB is limited (Safe et al., 1971).

Reactions of decachlorobiphenyl were recently described. Decachlorobiphenyl reacts as substituted pentachlorobenzene in nucleophilic substitution reactions occurring preferentially at the 4,4'-positions (Binns et al., 1971). Some of the reactions could possibly be developed into confirmatory tests in residue analysis. Thus decachlorobiphenyl yields a mixture of 4 and 4,4'-substituted nona- and octachlorobiphenyls on reduction with lithium aluminum hydride or butyl lithium. The reaction of decachlorobiphenyl with sodium methoxide in boiling pyridine yields a mixture of mono- and dimethoxy nona-, and octachlorobiphenyl.

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Many peaks in gas chromatograms of PCB and the lack of identification of individual chlorobiphenyls make the quantification of PCB difficult, since both height and area ratios of PCB peaks in environmental samples are usually different from those in commercial PCB preparations. Some authors use total peak area (Armour et al., 1970) or area under one (Koeman et al., 1969), two (Vermeer et al., 1970), or more peaks (Keil et al., 1971; Prestt et al., 1970), others use peak heights (Grant et al., 1971; Hansen et al., 1971; Risebrough, 1969). The values thus obtained are compared with values obtained in the same way on commercial PCB preparations (usually Aroclor 1254). A method based on the average electron-capture detector response to biphenyls containing from 1 to 7 chlorine atoms using commercial Aroclor preparations as standards, was recently described (Rote et al., 1971). The method is not more accurate than any of the other quantification procedures, since the detector response to chlorinated biphenyls with the same degree of chlorine substitution may vary significantly according to the substitution patterns (Zitko et al., 1971a). Although some believe that the quantification of PCB with any degree of confidence is impossible (Richardson et al., 1971), the general opinion is that the quantification is reasonably precise. The results obtained recently by different laboratories on an exchange sample of PCB, included in the O.E.C.D. pesticide monitoring program, have the same order of variability as usually occurs in the determination of chlorinated hydrocarbon pesticides (Holden, A. V., personal communication). However, because of the lack of individual chlorobiphenyl standards, the quantification cannot be accurate. No definite quantification procedure for PCB is developed and "laboratories are encouraged to exercise good judgment in their measurement of PCB residues and to explicitly describe the analytical procedures employed when reporting residues of PCB" (Burke, 1971).

During the analysis for PCB, great care must be taken to avoid contamination of samples, since PCB may be present in a variety of products. Thus PCB of the 40% chlorine variety were found in cardboard (Bailey et al., 1970) and in a wrapping plastic material (Mestres et al., 1970).

No analytical methods are available for the determination of halogenated biphenyls containing different halogens.

PCB are very likely metabolized by hydroxylation. Microbiological metabolism of biphenyl (Lunt et al., 1970) and the metabolism of 4-chlorobiphenyl in the rabbit (Block et al., 1959) have been described, and methods for the analysis of the phenolic metabolites of biphenyl (Raig et al., 1970) and of dichlorobiphenyl diol isomers (Tomori, 1970) by gas chromatography were developed. In the latter case, silylation was used to block the hydroxyl groups. On polyethylene glycol adipate the elution sequence was 3,3'-dichloro-, 3,5'-dichloro-, 5,5'-dichloro - 2,2'-dihydroxybiphenyl.

The constituents of Aroclor 1242, 1254, and 1260 have been recently identified by gas chromatography, NMR spectroscopy, and mass spectrometry. Aroclor 1254 yielded 69 constituents and the major components were identified to be 2,5-2',5'-, 2,3-2',5'- and 2,5-3',4'-tetrachlorobiphenyls, 2,5-2',3',6'-, 2,3-2',3',6'-, 2,5-2',4',5'-, 2,4-2',4',5'-, 2,5-2',3',4'-, 3,4-2',3',6'-, 3,4-2',4',5'-, and 3,4-2',3',4'-pentachlorobiphenyl, 2,3,6-2',4',5'-, 2,3,4-2',3',6'-, 2,4,5-2',4',5'-, and 2,3,4-2',4',5'-hexachlorobiphenyl. The fractionation of Aroclor 1242 and 1260 yielded 45 and 78 components, respectively. The most frequent substitutions in Aroclor 1242 occurred in positions 2-, 2,4-, and 2,5-. The structural features of Aroclor 1260 components were similar to those of Aroclor 1254 but the preparation contained more heptachlorobiphenyls (Sissons et al., 1971). Kovats retention index system (RI) was used to characterize PCB in this study. As already mentioned in terms of retention times, substitution in ortho positions decreases RI.

Chlorinated naphthalenes resemble PCB in industrial uses and chemical properties. Chlorinated naphthalenes accompany PCB on silicic acid chromatography (Armour et al., 1971).

Chlorinated naphthalenes are eluted in the same fractions as PCB (I and II) also on the alumina-silica chromatography of Holden and Marsden. If present alone or in a concentration comparable to that of PCB, their presence could possibly be recognized from the characteristic peak patterns on gas chromatography (see Appendix). UV spectrum of a commercial mixture of chlorinated naphthalenes has a maximum at 306 nm with an $A^{1\%}_{1cm}$ of 329 (see Appendix). PCB (Zitko, 1970) and polychlorinated terphenyls (PCT) have only negligible absorbance at this wavelength so that chlorinated naphthalenes could be confirmed in the presence of PCB and PCT by UV spectrophotometry. The limitation for this method is the background of UV-absorbing impurities eluted from alumina and silica columns and UV-absorbing compounds present in biological samples and eluted in fractions I and II.

PCT are not eluted from 5% DEGS-2% orthophosphoric acid (Reynolds, 1971) and SE-30 columns at 200°C. PCT (Aroclor 5460) can be determined by gas chromatography on a 6 ft x 4 mm glass column containing 3% OV-210 (Pierce Chemical Company) on Chromosorb WAW 60/80 and operated at 200°C. Under these conditions Aroclor 5460 gives 8 major peaks with retention times of 1.78, 2.45, 3.10, 3.96, 4.83, 5.88, 7.25, and 9.13 relative to decachlorobiphenyl, respectively. The electron-capture detector response to Aroclor 5460, based on the sum of heights of peaks 3.10, 3.96, and 4.83 is 0.122 per ng relative to decachlorobiphenyl. More than 90% of Aroclor 5460 is eluted in fraction II. Using this technique PCT were detected in some environmental samples and attempts are underway to confirm this finding by mass spectrometry (Zitko et al., 1971b).

Firemaster BP6 (hexabromobiphenyl) gives 7 peaks with retention times of 0.50, 0.88, 1.09 (major peak), 1.44, 1.77, 1.94, and 2.82 (major peak) relative to decachlorobiphenyl on the OV-210 column. In the pesticide cleanup chromatography the hexabromobiphenyl preparation is eluted in fractions I and II, the two major peaks being eluted mainly in fraction I (Zitko, V., O. Hutzinger, and P.M.K. Choi, unpublished).

The determination of chlorobenzene in water was described. The compound was extracted with methylene chloride and determined by gas chromatography (Martur et al., 1968). Chlorobenzene was removed from waste water by gravity separation, extraction with dichloromethane and adsorption on activated carbon. Residual dichloromethane was removed by aeration (Radvinskii et al., 1969).

Methods for the determination of carbon tetrachloride in water were reviewed and a method based on the extraction of carbon tetrachloride with methyl ethyl ketone and its color reaction with pyridine in an alkaline medium was suggested (Stankovic, 1965).

The presence of nonvolatile organochlorine compounds which cannot be determined by gas chromatography in hexane extracts of environmental samples could be detected by the decomposition of samples with metallic sodium and determination of chloride as described for some chlorinated hydrocarbon pesticides (Koblitsky et al., 1962).

A semi-quantitative method for the detection of less-volatile lipophilic chlorine compounds by circular TLC and development with silver nitrate was described (Koppe et al., 1970a).

PCB levels in the aquatic environment

The presence of PCB in the environment has been unequivocally established. Of major interest at the moment are comparisons of PCB levels in different geographical areas and the sources and transport mechanisms of PCB in the environment. Levels of PCB in fish, seals, and birds are summarized in Tables I and II. PCB levels in eggs of aquatic birds from the Bay of Fundy and Passamaquoddy Bay are presented in Table III. Some of the data have already been mentioned in the PCB reviews, but are presented again for comparison purposes.

The analyses of fish indicate ubiquitous occurrence of PCB, with higher levels in fish from coastal areas and enclosed bodies of water such as Gulf of Maine-Bay of Fundy, Archipelago of Stockholm, and the Baltic Sea. Relatively fewer data are available for freshwater fish but is very likely that the trend is similar, and fish from localities close to industrialized areas and population centers contain elevated levels of PCB. The accumulation of PCB in the food chain is indicated by the

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levels of PCB found in seals and in aquatic birds. The levels of PCB in eggs of cormorants, herring gulls, and black ducks from the Bay of Fundy and from Passamaquoddy Bay are surprisingly high and so are the levels in the body tissues of one cormorant and one herring gull from this area. The other herring gull, found dead on Hospital Island has lower residues of PCB and p,p'-DDE in the tissues. This indicates that there may be a considerable variation of PCB levels between individual specimens. The concentration of PCB in one cormorant from The Netherlands is very high.

It is interesting to note that PCB and p,p'-DDE are present practically exclusively in the yolk. For example, D.C. cormorant eggs from Station F contain 92.5 µg/g of PCB and 61.8 µg/g of p,p'-DDE in the yolk, while only 1.37 µg/g of PCB and 0.77 µg/g of p,p'-DDE were found in egg-white.

The toxicological significance of PCB levels in the environment cannot be evaluated at the moment.

The levels of organochlorine pesticides and PCB in fish, margarine, vegetable oils, and other products from Sweden have been reported (Westöö et al., 1970a,b). Data on some terrestrial and aquatic organisms from Norway were published (Bjerk et al., 1970).

Three samples of commercial dry fish food, analysed in this laboratory contained 0.15, 0.13, and 0.25 µg/g of PCB, respectively. This may represent an important source of PCB in laboratory- and hatchery-reared fishes. For example, one-year-old Atlantic salmon parr, reared at this Station contained 0.20 µg/g of PCB in liver and 0.88 µg/g in caeca, while small parr contained 0.30 µg/g (whole fish). Hatchery-reared rainbow trout (Salmo gairdneri), held at the Station for experimental purposes, contained 0.14, 0.22, and 1.49 µg/g of PCB in muscle, liver, and caeca, respectively. (All concentrations are given on wet weight basis). The tissues of both salmon and trout contained only traces of p,p'-DDE. The levels of PCB may be significant if the fish are used in testing sublethal effects of PCB and other pollutants.

Three samples of Canadian margarine were analysed in this laboratory and PCB concentrations found were 0.47, 0.21, and 0.18 µg/g for margarine containing 80% marine oils, 60% marine oils, and 100% vegetable oils. The levels of p,p'-DDE were 0.07, 0.25, and less than 0.01 µg/g, respectively.

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Table I. PCB and chlorinated hydrocarbon pesticides in fishes and fish-eating birds.

Species	Location	PCB, μg/g	p,p'-DDE, μg/g	Other
Bluefin tuna (muscle)	California	0.04*	0.25*	
Thunnus thynnus (liver)		0.04*	0.09*	
(muscle)	New Jersey	0.36**	0.04**	
Yellowfin tuna (liver)	Galapagos	<0.01*	0.01*	
Thunnus albacares (")	Central America	0.04*	0.19**	
(")	West Africa	0.17**	0.03**	
Skipjack tuna (liver)	Hawaii	0.10*	0.01*	
Euthynnus pelamis				
(muscle)	Hawaii	<0.01*	0.01*	
(liver)	Galapagos	<0.01*	<0.01*	
(liver)	Ecuador	<0.01*	<0.01*	
(muscle)	New Jersey	0.82**	0.12**	
(muscle)	West Africa	0.14**	0.02**	
Bluefish (muscle)	New Jersey	0.84**	0.17**	DDT 0.07**
Pomatomus saltatrix				
Swordfish (muscle)	Cay Sal Bank	0.22**	0.02**	
Xiphias gladius				
Blue marlin (muscle)	Walker's Cay	0.16**	0.06**	
Makaira nigricans				
Northern anchovy (whole fish)	California	1.00*	11.6*	
Engraulis mordax				
Herring (whole fish)	Eastern Canada	0.40***	0.13***	DDT 0.09***
Clupea harengus (muscle)	Baltic Sea	0.27+	0.28+	DDT 0.40+
	Archipelago of Stockholm	0.17+	0.12+	DDT 0.11+
	Gulf of Bothnia	0.06+	0.12+	DDT 0.14+
Sprat (whole, dry wt. basis)	Dutch Wadden Sea	0.3-2.0'		
Clupea spratius				
Pacific jack mackerel (whole fish)	California	0.02*	0.32*	
Trachurus symmetricus				
Mackerel (muscle)	Bay of Fundy	0.35***	0.07***	
Scomber scombrus				

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(Table I Cont'd)

Species	Location	PCB µg/g	p,p'-DDE µg/g	Other
Shiner perch (whole fish) *Cymatogaster aggregata*	California	0.90*	0.37*	
English sole (whole fish) *Parophrys vetulus*	California	0.08*	0.18*	
Plaice (muscle) *Hippoglossoides platessoides*	Nova Scotia Banks	0.03***	0.01***	
	Bay of Fundy	0.38**	0.01**	
Plaice (muscle) *Pleuronectes platessa*	Swedish West Coast	0.02+	<0.01+	
(muscle)	Baltic Sea	0.02+	<0.01+	
Hake (whole fish) *Merluccius productus*	California	0.12*	0.12*	
White hake (muscle) *Urophycis tenuis*	Nova Scotia Banks	0.02***	0.02***	
	Bay of Fundy	0.44**	0.03**	
Ocean perch (muscle) *Sebastes marinus*	Nova Scotia Banks	<0.01***	<0.01***	
	Bay of Fundy	0.32**	0.03**	
Cod (muscle) *Gadus morhua*	Nova Scotia Banks	0.02***	0.01***	
	Bay of Fundy	0.55**	0.04**	
(muscle)	Swedish West Coast	0.02+	<0.01+	
(muscle)	Baltic Sea	0.03+	0.03+	
Sea raven (muscle) *Hemitripterus americanus*	Bay of Fundy	0.21**	0.08**	
(viscera)	Bay of Fundy	0.73**	0.30**	DDT 0.24**
Picked dogfish (muscle) *Squalus acanthias*	Swedish West Coast	0.15+	0.06+	
Atlantic salmon *Salmo salar* (muscle)	Eastern Canada	0.45**	0.22**	
(muscle)	Tagged in Canada, (caught in Greenland)	0.20**	0.04**	
Smolt (whole fish)	Eastern Canada	0.10**	0.28**	

.07**

.09***
.40+

.11+
.14+

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(Table I Cont'd)

Species	Location	PCB µg/g	p,p'-DDE µg/g	Other
Adult salmon	Eastern Canada			
(muscle)		0.62**	0.07**	
(liver)		0.84**	0.14**	
(caeca)		0.65**	0.12**	
(ovaries)		0.71**	0.11**	
(testes)		0.37**	0.04**	
(muscle)	Baltic Sea	0.30+	1.9+	DDT 1.5+
Commercial fish oil	Eastern Canada	3.55**	2.27**	DDT 0.37**
	Baltic Sea	3.5+	8.7+	DDT 7.3+
	Swedish West Coast	0.74+	0.9+	DDT 1.2+
Cod liver oil	O.E.C.D. test	1.39•	0.51•	DDT 1.44•
Mussel (whole)	Swedish West Coast	0.08+	0.01+	
Mytilus edulis	Baltic Sea	0.03+	0.01+	
	Archipelago of Stockholm	0.04+	0.02+	
	Eastern Canada	0.14***	0.02***	
	Finland	0.06•	traces	
	Holland	0.4•		
	Norway	traces		
	Sweden	0.03•		
Dogfish	Norway	0.01-0.04•		
Squalus acanthias	Sweden	0.15•		
Coho salmon Oncorhynchus kisutch	Lake Michigan	14.6++	10.4++	DDT 3.2++
Flounder (Paralichthys sp.)	Escambia Bay	4.5+++		
Croaker Micropogon undulatus	Escambia Bay	12+++		
Menhaden Brevoortia patronus	Escambia Bay	11+++		
Pinfish Lagodon rhomboides	Escambia Bay	10+++		
Speckled trout Cynoscion nebulosus	Escambia Bay	20+++		
Shrimp Penaeus setiferus and aztecus	Escambia Bay	1.5-2.5+++		

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(Table I Cont'd)

Species	Location	PCB µg/g	p,p'-DDE µg/g	Other
Blue crab *Callinectes sapidus*	Escambia Bay	1.7+++		
American eel (muscle) *Anguilla rostrata*	Eastern Canada	0.71***	0.50***	
(liver)		0.57***	0.19***	
Chain pickerel (muscle) *Esox niger* (liver)	Eastern Canada	0.33***	0.16***	
		4.93***	2.38***	DDT 0.63**
Pike *Esox lucius*	Holland	0.05•		
	Norway	traces•		
	Sweden	0.02•		
Seal (blubber) *Phoca vitulina* and *Halichoerus grypus* (blubber)	Baltic Sea	15+	34+	DDT 32+
	Archipelago of Stockholm	6.1+	31.8+	DDT 4.2+
Grey seal pups (blubber) (on lipid basis)	S.W. England	1800=	65=	DDT 37=
	N.E. England	50=	8.4=	7.1=
	Sable Island	12=	5.4=	5.4=
	Orkney Islands	7.9=	3.1=	3.1=
Grey seal adults	Sable Island	20=	22=	17=
	Orkney Islands	17=	4.7=	5=

*Risebrough, 1969

**This report

***Zitko, 1971b

+Jensen et al., 1969

•Holden, 1970c

++Armour et al., 1970

+++Duke et al., 1970

=Holden, 1970b

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Table II. PCB and p,p'-DDE in birds.

Species		Location	µg/g PCB	µg/g p,p'-DDE
Brandt's cormorant *Phalacrocorax penicillatus*	(eggs)	Farallon Island	113[++]	326[++]
Pelagic cormorant *P. pelagicus*	(eggs)	California	62[++]	128[++]
Bulked shag *P. aristotelis*	(eggs)	Britain, West Coast	5[++]	2.2[++]
		Britian, East Coast	3[++]	1.6[++]
D.C. cormorant *P. auritus*	(eggs)	North Dakota	3-4[=]	3-4[=]
		Wisconsin	25[=]	44[=]
		Manitoba	18[=]	20[=]
		Western Canada	0.67-2.21[•]	3.3-3.5[•]
California gull *Larus californicus*	(eggs)	Alberta	0.87[+=]	7.26[+=]
		Western Canada	1.57-1.74[•]	2.9-21.8[•]
Razor bill *Alca torda*	(eggs)	Britain, West Coast	7[++]	
		" East Coast	6[++]	
Kittiwake *Rissa tridactyla*	(eggs)	" West "	8[++]	
		" East "	3[++]	
Mallard duck *Anas platyrhynchos*	(eggs)	Western Canada	0.09[•]	0.2[•]
Guillemot *Uria aalgae*	(eggs)	Britain, West Coast	8[++]	2.0[++]
		" East "	3[++]	0.7[++]
		Baltic Sea	16[••]	38.8[••]
White pelican *Pelecanus erythrorhynchos*	(eggs)	North Dakota, Saskatchewan	2[=]	1[=]
		California	8-12[•••]	76-135[•••]
		South Carolina	8-12[•••]	11[•••]
		Florida	3-8[•••]	2-7[•••]
Common tern *Sterna hirundo*	(eggs)	Western Canada	0.94-1.57[•]	5.1-33.3[•]
Great Blue Heron *Ardea herodias*	(eggs)	Western Canada	trace-3.41[•]	3.7-78.0[•]

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(Table II cont'd)

Species		Location	µg/g PCB	µg/g p,p'-DDE
Whitetailed eagle *Haliaeetus albicilla*	(Pect. muscle)	Archipelago of Stockholm	190••	330••
Heron *Ardea cinerea*	(Pect. muscle)	Archipelago of Stockholm	9,400••	14,000••
Common cormorant *P. carbo*	(total body)	The Netherlands	402**	14.3**
D.C. cormorant *P. auritus*	(muscle)	Passamaquoddy Bay	3.38***	8.40***
	(liver)		2.13***	4.16***
	Subcutaneous fat		38***	164***
	Abdominal fat		52***	162***
Herring gull° *L. argentatus*	(muscle)	Passamaquoddy Bay	5.06***	2.07***
			(2.69***)	(0.75***)
	(liver)		6.50***	2.08***
			(1.93***)	(0.66***)
	Subcutaneous fat		75***	26***
			(16.2***)	(7.95***)
	Ovaries		6.24***	1.68***
Eider° *Somateria mollissima*	(liver)	The Netherlands 1967	5.5*•	0.14*•
			(63*•)	(2.59*•)
		1968	5.6*•	1.4*•
			(89*•)	(7.2*•)
California gull *L. californicus*	(abdominal fat)	Western Canada	23-62.6•	138-416•
	" "	Alberta	18.87+=	134+=
	(brain)	Western Canada	0.81•	3.6•
		Alberta	0.29+=	1.31+=
	(liver)	Western Canada	1.69•	15.7•
		Alberta	0.79+=	5.37+=
	(ovary)	Western Canada	2.52•	22.9•
		Alberta	1.22+=	12.56+=

+µg in whole egg

*Risebrough, 1969

++Prestt et al., 1970

=Anderson et al., 1969

+=Vermeer et al., 1970

°Shot and (dead or dying), respectively

•Reynolds, 1971

••Jensen et al., 1969

•••Mulhern et al., 1971

**Analysed in this laboratory: an O.E.C.D. exchange sample

***this report

*•Koeman et al., 1970

Table III. PCB and p,p'-DDE in eggs of aquatic birds (μg/g wet weight) from the Bay of Fundy and Passamaquoddy Bay, New Brunswick (this report).

	Eggs		Nests			
	No.	Av.weight,g	No.	Stn.	PCB	p,p'-DDE
D.C. Cormorant	11	47.0	11	F	43.5±2.6*	29.4±8.5*
(P. auritus)	4	39.3	4	P	17.2±0.79	8.63±1.25
Herring gull	10	99.1	6	F	12.6±6.1	5.67±3.03
(L. argentatus)	3	80.8	3	P	5.54±0.97	2.83±0.31
Black duck (Anas rubripes)	4	105.6	4	F	9.10±0.53	1.50±0.20
Guillemot (Uria aalgae)	1			F	2.02	4.34

*Standard deviation

F = Fatpot Island

P = Hospital Island

PCB in humans

Fatal poisoning of more than 644 people and fatal edema of 400,000 chicks occurred in Western Japan in 1968 due to contamination of edible rice bran oil and acidulated oil by chlorobiphenyl used as the heat-transfer medium in oil refining (Takeshita et al., 1970). Main components of the commercial PCB preparation KC-400 (Kaneclore 400), were 2,4,3',4'-, 2,5,3',4'-, 2,3,4,4'-, and 3,4,3',4'-tetrachlorobiphenyl, and 2,3,4,3',4'-pontachlorobiphenyl (Saeki et al., 1971).

The contaminated rice oil contained about 2300 ppm of PCB. New-born and still-born infants born from poisoned mothers had darkish skin, possibly due to the presence of PCB which pass through the placental barrier and accumulate in the skin of the fetus (Kojima et al., 1969). A symposium report on the poisoning has been published (Inagami et al., 1969).

The components of KC-400 with longer retention times were detected in sputa and fatty tissues of patients (Kojima, 1971). Serum triglyceride, cholesterol, and phospholipid concentrations were highly increased, and the lecithin-cholesterol acyltransferase activity was decreased. Plasma lipoprotein lipase activity

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was decreased in female patients (Uzawa et al., 1971; Nagai et al., 1969). About 40% of the examined patients showed an elevated excretion of steroids. The 17-keto-steroids tended to increase in male and decrease in female patients (Nagai et al., 1971).

Some of the patients died about one year after the accident. PCB with longer retention times, probably pentachloro- and higher chlorinated biphenyls were still, after more than 8 months, found in their tissues and their presence might have been responsible for the long duration of the intoxication symptoms (Kojima et al., 1970).

In Europe, PCB were detected in human milk in a concentration of 0.103 µg/ml or 3.5 µg/g milk fat. Human fatty tissue contained 5.7 µg/g of PCB. Hexachlorobenzene was present in milk in a concentration of 0.153 µg/ml (5.3 µg/g fat) and the level of hexachlorobenzene in the fatty tissue was 6.3 µg/g (Acker et al., 1970). Hexachlorobenzene was recently detected in human serum (Zeman et al., 1971).

In the U.S.A., two human adipose tissue samples were reported to contain 200 and 600 ppm of PCB, respectively, as determined by gas chromatography and confirmed by mass spectrometry (Biros et al., 1970).

PCB were as toxic to human cells in tissue culture as DDT (Litterst et al., 1971).

Metabolism and physiological effects of halogenated hydrocarbons

Halogenated hydrocarbons, particularly chlorinated hydrocarbons, are usually metabolized in animals by dehalogenation. Halogen atoms may be replaced either by cysteine, the N-acetyl-cysteine (mercapturic acid) derivative being excreted in the urine, or by hydroxyl. In the latter case the hydroxylated derivative is either excreted as such or in the form of its glucuronide. If several halogens are removed from one aliphatic carbon atom, aldehydes (such as formaldehyde in the case of bromochloromethane) or acids (DDA from DDT) are the excreted products. Bacteria and possibly mammals are able to carry out reductive dechlorination of chlorobenzenes and, probably, both insects and mammals can dehydrochlorinate chlorinated compounds. Examples of this reaction are the formation of DDE from DDT and pentachlorocyclohexene from γ-hexachlorocyclohexane (Smith, 1964).

Bacteria contain halidohydrases catalyzing the dehalogenation of halogenated fatty acids (Goldman et al., 1968). Hepatic microsomes of rabbit, rat, and guinea pig contain an enzymic system dechlorinating chloroethanes and chloropropanes (Van Dyke et al., 1971). This system requires NADPH and oxygen, is inducible by phenobarbital and benzpyrene, and has a considerable substrate specificity. Thus 13.5, 6.0, and <0.5% of chlorine was enzymically removed from 1,1-dichloro-, 1,1,2,2-tetrachloro-, and

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1,2-dichloroethane, respectively. In the chloropropane series, 40.8, 24.6, 5.8, 5.2, 3.2, and 2.5% of chlorine was removed from 1,1,2-trichloro-, 1,1-dichloro-, 1,2-dichloro-, 2-chloro-, 1-chloro-, and 2,2-dichloropropane, respectively.

Very little information is available on the metabolism of PCB. Varying peak ratios observed on gas chromatograms of PCB extracted from different tissues and from animals at different trophic levels suggest that some selective metabolism of individual chlorinated biphenyls takes place.

When rabbits were fed 4-chlorobiphenyl, 4-(p-chlorophenyl) phenol was isolated from ether-soluble fraction of urine, and 4-chlorobiphenylglucosiduronide from the ether-soluble fraction of urine. Analogous metabolites were found in rabbits fed biphenyl and the study indicated that 4-chlorobiphenyl was metabolized as readily as biphenyl by the rabbit, but twice as much 4-chlorobiphenyl as biphenyl was excreted in the form of glucuronic acid glycoside (Block et al., 1959). Rabbits can metabolize 1-chloro- and dichloronaphthalene and in both cases, a glucosiduronic acid derivative is the major metabolic product. No metabolic products of more highly chlorinated naphthalenes were detected and it was suggested that higher degree of chlorination may interfere with the metabolism. There is a correlation between the extent of chlorinated naphthalenes metabolism and toxicity. Naphthalenes containing 5 or more chlorine atoms produced severe toxic symptoms (Cornish et al., 1958).

It is possible that the metabolism of PCB follows similar patterns, i.e., lower chlorinated PCB are metabolized and excreted while higher chlorinated PCB are not metabolized.

PCB containing up to 48% chlorine had estrogenic activity as determined by the 18-hr glycogen response of the rat uterus. Minimum effective dose was 8 mg, which is more than the effective dose of p,p'-DDT, o,p'-DDE (4 mg), and o,p'-DDT (0.25 mg), and equal to the activity of o,p'-DDMU. Aroclor 1254, 1260, 1262, and 1268, Aroclor 4465 and 5460 were inactive, Aroclor 1221, 1232, 1242, and 1248 were active at 8 mg, and Aroclor 5442 was active at 1 mg level; p,p'-DDD, p,p'-DDE, p,p'-DDMU, p,p'-DDA, and o,p'-DDD were inactive. Apparently, the requirement for estrogenic activity are unsubstituted, and either -OH or -OCH_3 substituted p,p'-positions (Bitman et al., 1970). Administration of PCB to rabbits increases the total lipid, triglyceride, and cholesterol content of liver and decreases the total liver phospholipid content. The concentration of serum triglycerides is abnormally increased (Ito et al., 1971).

The enhancement of the liver drug-metabolizing enzyme system in the rat by several individual chlorinated biphenyls was studied. The most potent inducer was 2,3',4,4',5-

pentachlorobiphenyl. The effect induced with a single dose of 3,3',4,4'-tetrachlorobiphenyl continued for 6 weeks (Fujita et al., 1971).

Aroclor 1254 at a daily dose of 10 mg/kg (28 days) caused increased liver weights, and carboxylesterase, aniline hydroxylase, and aminopyrine-N-demethylase activities in rabbits. No effect on body weight and on number of fetuses/litter was observed. Doses of 12.5, 25, and 50 mg/kg were embryotoxic (Villeneuve et al., 1971). Acute oral LD50 of PCB in mice is about 2.0 g/kg. Daily dose of 0.1 g/kg administered to mice for 4 weeks caused a decrease in body weight and a 10-fold increase in serum triglycerides (Tanaka et al., 1969).

Polychlorinated biphenyls of the KC-400 variety were administered in a single dose to mice (2.0 mg/mouse). The concentration of PCB in the skin, one day after the ingestion was twice as high as that in the liver. Tetrachlorobiphenyls were almost completely eliminated from the tissues in 3-4 weeks but small amounts of penta- and hexachlorobiphenyls were still detectable after 9-10 weeks (Yoshimura et al., 1971). Aroclor 1254 was found to potentiate the toxicity of carbon tetrachloride in the rat (Grant et al., 1971). Mice receiving PCB of the 48% chlorine variety for up to 26 weeks and cynomolgus monkeys (about 1 kg body wt.) receiving 641 mg of PCB in 40 days or 348 mg in 239 days developed enlarged livers. An increase of smooth-surfaced membranes and reduction of rough-surfaced membranes of the endoplasmic reticulum was observed (Nishizumi, 1970).

The distribution of PCB in rats dosed with PCB was determined by X-ray fluorescence analysis. PCB residues were found mainly in the skin, and to a lesser extent in muscles, intestines, livers, pancreas, and lungs. The gas chromatographic patterns of PCB varied from tissue to tissue (Sekita et al., 1970). Distribution, storage and excretion of PCB by Sherman rats was reported (Curley et al., 1971). Feeding PCB of the Aroclor 1242 variety depressed Vitamin A in rat liver by about 40% (Cecil et al., 1971).

PCB produced porphyria in chickens fed 400 ppm of Phenoclor DP6, Clophen A60, and Aroclor 1260 in the diet. The first 2 preparations were much more toxic than Aroclor 1260 and had higher incidence of edema and liver necrosis. PCB levels in the liver could not be correlated with the survival time and a great variation in the residue levels in liver and brain was observed (Vos et al., 1970a). It was reported that PCB reduce estrogen concentration in ring doves (Streptopelia risoria) and cause thin-shelled eggs (Peakall, 1970). However, according to a later paper, no eggshell thinning by Aroclor 1254 was found in ring doves fed 10 ppm of Aroclor 1254 in their diet for 6 months. After 35 days on the diet, the level of PCB in the eggs was 4.81±1.08 ppm (Peakall, 1971). Aroclor 1254 did not induce measurable changes in egg shells or in the reproductive success of mallard ducks (Anas platyrhynchos) and bobwhite (Colinus virginianus) receiving 25 and 50 ppm of Aroclor in ad libitum diet. LC50's (ppm in ad libitum diet) of Aroclor 1242, 1248, 1254, 1260, and 1262 for mallards were 3180, 2795, 2700,

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1975, and 3010, as compared to 3570, 1870, 200, and 22 for DDE, DDT, dieldrin, and endrin, respectively (Heath et al., 1970). Similar data for pheasants (Phasianus colchicus), Japanese quail (Coturnix coturnix), and bobwhite were also presented. About 4-fold difference in PCB toxicity to different species was noticed. Thus for example LC50 of Aroclor 1254 is 1090, 605, and 2900 for pheasant, bobwhite, and Japanese quail, respectively. The toxicity of Aroclor 1254 to Bengalese finch (Lonchura striata) is only about 1/13 of the toxicity of DDT, however, Aroclor 1254 has a much more gradual toxicity curve. No correlation was found between the dose and concentration of PCB in the liver. It was suggested that lethal poisoning of birds in Britain by PCB was unlikely, however, breeding failure was possible (Prestt et al., 1970).

Mallard ducklings survived 10 days of feeding on a diet containing 25, 50, and 100 ppm of PCB but suffered significantly higher mortality than control animals when later infected with duck hepatitis virus (Friend et al., 1970).

PCB (Clophen A50) enhanced nocturnal activity of robins (Erithacus rubecula). Control birds contained from 0.05 to 0.12 μg/g PCB on fresh weight basis in breast muscle. Birds fed PCB (ingested amount 55-65 μg) contained 0.16-0.47 μg/g in breast muscle (Ulfstrand et al., 1971).

Fiddler crabs (Uca pugilator) and pink shrimp (Penaeus duorarum) were shown to accumulate PCB from contaminated sediment particles (Nimmo et al., 1971). Lethal threshold of Aroclor 1254, solubilized in water by a commercial nonionic dispersant formulation, to Gammarus oceanicus was 0.001-0.1 mg/l (Wildish, 1970). Branchial necrosis was observed. Uptake of Aroclor 1254 from sea water by G. oceanicus was measured (Wildish et al., 1971).

Pinfish (Lagodon rhomboides) and spot (Leiostomus xanthurus) died after exposure to 5 ppb of Aroclor 1254 for 14-45 days. Aroclor 1254 levels in exposed fish were 46-152 ppm. After 84 days fish eliminated 73% on ppm basis and 61% on total body burden basis (Hansen et al., 1971).

Fatty livers were frequently observed in salmon reared in Swedish hatcheries and one-year-old salmon, average weight 18 g, had 42.2 ppm on fat basis of PCB in the liver. Eggs from salmon grown at sea contained 7.7-9.2 ppm of PCB after stripping and 7.7-19 ppm after about 3 months incubation in fresh water. The figures for freshwater-reared females were 7.7-19 and 14-34 ppm (all on fat basis, fat content is 3.8-7.9%), respectively. High losses of eggs could be correlated with high PCB levels. The losses were due to either unfertilized eggs or to mortality at an early stage (Johansson et al., 1970).

Aroclor 1242 in a concentration of 0.1 ppm inhibited the growth of C. closterium (Keil et al., 1971).

Latent toxicity of PCB to Chorthippus brunneus at the moult was suggested (Moriarty, 1969).

Two compounds, 3-chloro-2-hydroxy-, and 5-chloro-2-hydroxybiphenyl were repellent to Musca domestica (Shambaugh et al., 1968). The latter was also effective against Tetrachynus telarius. 3-chloro-2-hydroxy-5-nitrobiphenyl is an uncoupler of oxidative phosphorylation (Cheng et al., 1969).

Activity of DNase I is inhibited by 2-hydroxy- and 3,4-dihydroxybiphenyl, while 4,4'-dihydroxybiphenyl has no effect (Gottesfeld et al., 1971).

Fatty livers are the general symptom of exposure to vapours of chlorinated hydrocarbons such as carbon tetrachloride and 1,1,2,2-tetrachloroethane. The increase of the hepatic triglyceride content has a maximum between 20 and 25 hours after exposure while the concentration of plasma triglycerides increases between 70 and 90 hours (Tomokuni, 1970).

o-dichlorobenzene is more toxic to mammals than p-dichlorobenzene. Accumulation of chlorobenzene and o-dichlorobenzene but not of p-dichlorobenzene was observed in experimental animals. Threshold concentrations for the odour and taste of water are for chlorobenzene 0.02 mg/l, for o-dichlorobenzene 0.002 and 0.0001 mg/l, and for p-dichlorobenzene 0.002 and 0.006 mg/l, respectively (Varshavskaya, 1967). Primary metabolites of p-dichlorobenzene are 2,5-dichlorophenol and 2,5-dichloroquinol, excreted in the urine as glucuronide and ethereal sulfate conjugates. A method for their determination by gas chromatography of their trimethylsilyl derivatives was described (McKinney et al., 1970).

The toxicity of chlorobenzenes to fish increased with increasing chlorine substitution, provided the compounds were water soluble; 1,2,4-trichlorobenzene was most toxic to Barbus conchonius (Toman et al., 1959). The determination of hexachlorobenzene in grain by gas chromatography was described (Taylor et al., 1970). Half-life of hexachlorobenzene in Japanese quail was about 3 weeks (Vos et al., 1968).

The no-effect level of hexachlorobenzene in Japanese quail (Coturnix coturnix japonica) was 1 ppm in an ad libitum for 90 days' administered diet. Slight liver damage and enlarged fecal excretion of coproporphyrin was observed in animals fed 5 ppm of hexachlorobenzene in the diet. The hexachlorobenzene levels in liver and brain were 0.79 and 0.47 ppm, 2.13 and 2.32 ppm in females and males at the 1 ppm level, respectively; 6.88 and 0.99 ppm, 8.56 and 1.44 ppm at the 5 ppm level. Liver residues of hexachlorobenzene in sparrow hawk (Accipiter nisus), buzzard (Buteo buteo), and hooded crow (Corvus cornix) from The Netherlands averaged 45.5 ppm during 1965-1968, and the average in 1968-1969 for the above species and Kestrel (Falco tinnunculus), marsh harrier (Circus

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aeruginosus), barn owl (Tyto alba), long-eared owl (Asio otus), and crane (Grus grus) was 48.2 ppm (Vos et al., 1971).

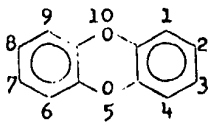
Hexachlorobutadiene caused skin irritation and hyperemia in rats (LD50 4.33 g/kg), and its oral LD50 was 165 mg/kg (Chernokan, 1967). Hexachlorocyclopentadiene inhibited biochemical oxidation in water in a concentration of 0.5 mg/l, and a concentration of 0.0015 mg/l produced detectable smell. Maximum permissible concentration of 0.001 mg/l was suggested (Neistein et al., 1965). Contact eczema was caused by manipulation of timber treated with Xylamon®, a wood-protecting agent containing chlorinated naphthalenes (Weichardt, 1970).

Lipid-bound bromine was detected in the adipose tissue of rats fed brominated maize oil (BMO). At dietary levels of 0.05, 0.2, and 0.8% BMO, adipose tissue contained 60, 200, and 1050 mg/100 g lipid-bound bromine. The brominated compounds were not metabolized as normal lipid. Rats fed 0.8% BMO for 6 weeks contained 730 mg/100 g lipid-bound bromine in the adipose tissue. When returned to control diet, the bromine content after one week was 830 in the group fed ad libitum and 2650 in the group with restricted feeding. After two weeks the values were 740 and 5350, respectively (Gaunt et al., 1971a). Lipid-bound bromine was found in adipose tissue, liver, spleen, adrenals, brain, kidneys, and lymph nodes of pigs fed BMO. None was detected in serum and urine (Gaunt et al., 1971b).

Tetra- and pentachlorodibenzofurans were detected in certain commercial PCB preparations (Clophen, Phenoclor). The level of the latter was about 5 ppm in Clophen and about 20 ppm in Phenoclor (Vos et al., 1970b). These compounds are extremely toxic. Tri- and tetrachlorodibenzofuran causes often lethal necrosis of the liver in rabbits after a single oral dose of 0.5-1.0 mg/kg, and a structurally similar 2,3,7,8-tetrachlorodibenzo-p-dioxin is effective in a single oral dose of 0.05-0.1 mg/kg (Vos et al., 1970b loc. cit.).

Determination of chlorinated dibenzo-p-dioxins and dibenzofurans

Chlorinated dibenzo-p-dioxins are byproducts in the preparation, hydrolytic, and pyrolytic reactions of chlorophenols.



Structurally somewhat similar to chlorinated dibenzofurans, mentioned earlier, these compounds, also known as "chick edema factor" are extremely toxic.

Recently their presence in technical 2,4,5-T received publicity (Dow Chemical Company, 1970) and a method for the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in technical 2,4,5-T was developed (Storherr et al., 1971). The compound was separated by steam distillation and determined by microcoulometric gas chromatography. Over 100 samples of 18 different pesticides derived from chlorophenols were analyzed for TCDD. Seventy-six percent of the samples contained less than 0.1 μg/g of TCDD, 7% contained between 0.1 and 1.0 μg/g and 9% contained more than 10 μg/g (Woolson et al., 1971). Three out of 6 commercial samples of 2,4,5-trichlorophenol contained TCDD, 0.07, 1.4, and 6.2 ppm, respectively. TCDD was absent from 11 examined samples of tetra- and pentachlorophenol. These samples, however, contained hexa-, hepta-, and octachlorodibenzo-p-dioxins, and a variety of chlorofurans and chloroethers. All pentachlorophenols examined contained from 0.17 to 39 ppm of hexachlorodibenzo-p-dioxins, 2 pentachlorophenol preparations probably contained a hexachlorohydroxybiphenyl. Electron-capture gas chromatography and combined gas chromatography - mass spectrometry were used to detect all above-mentioned compounds (Firestone et al., 1971a).

TCDD was not generated in soils containing 2,4-dichloro- and 2,4,5-trichlorophenol, but 80-85% of added TCDD was recovered from the soil after 160 days (Kearney et al., 1971).

Some of the lower chlorinated dibenzo-p-dioxins behave similarly to PCB and a separation of 2,3-dichloro-, 2,3,7-trichloro-, and 2,3,7,8-tetrachlorodibenzo-p-dioxin from PCB was described (Porter et al., 1971). Column chromatography on alumina, activated at 130°C overnight was used. PCB were first eluted with 1% methylene chloride in hexane and the chlorodibenzo-p-dioxins were eluted with 20% methylene chloride in hexane. Because of the extreme toxicity of these compounds, it is unlikely that standards will be widely available. The retention times relative to aldrin on a 6 ft - 4 mm column containing 3% OV-101 on 80/100 mesh Chromosorb WHP were 0.93, 1.67, and 3.0 for 2,3-dichloro-, 2,3,7-trichloro-, and 2,3,7,8-tetrachlorodibenzo-p-dioxin, respectively. The most common standard for hexa-, hepta-, and octachlorodibenzo-p-dioxin is 1.5% reference toxic fat (available from Division of Pesticides, Food and Drug Administration, Washington, D.C., 20204).

The determination of hexa-, hepta-, and octachlorodibenzo-p-dioxin in tissues of chickens, fed the toxic fat, was described. Over 90% of the ingested higher chlorodibenzo-p-dioxins was excreted. About one-half of the absorbed dioxins was present in the liver (Firestone et al., 1971b). In this

Table IV. Retention time and electron-capture detector response of chlorinated dibenzofurans and dibenzo-p-dioxins.

Compound	Retention time (cm)	Response/ng Height	Response/ng Area
4% SE-30 Column			
Dichlorodibenzofuran	1.65	0.67	1.18
Trichlorodibenzofuran	3.35)	0.63	3.36
Tetrachlorodibenzofuran	6.80)		
Pentachlorodibenzofuran	13.5*		
Hexachlorodibenzofuran	27.6*		
Heptachlorodibenzofuran	55.0*		
Octachlorodibenzofuran	80		
2,7-dichlorodibenzo-p-dioxin	1.90*	0.28	0.49
trichlorodibenzo-p-dioxin	3.64*		
2,3,7,8-tetrachlorodibenzo-p-dioxin	7.35	0.043	0.25
pentachlorodibenzo-p-dioxin	12.3*		
hexachlorodibenzo-p-dioxin	22.8 25.3	0.23	4.11
heptachlorodibenzo-p-dioxin	43.6*		
octachlorodibenzo-p-dioxin	83		
p,p'-DDE	3.95	6.03	16.3
3% OV-210 Column			
Octachlorodibenzofuran	4.05	0.22	
Hexachlorodibenzo-p-dioxin	1.40 1.60	0.13	
Octachlorodibenzo-p-dioxin	4.30	0.23	
Decachlorobiphenyl	1.60	1.75	

*Estimated from log(retention time) vs number of chlorine atoms plots.

Retention times of Aroclor 1254 peaks on the SE-30 Column were:

(1.95), 2.90, 3.45, (4.30), 5.15, 6.05, 7.20, (8.40), (10.1), (11.5), and (13.7)

In brackets are retention times of peaks not used for quantification.

All evaporations were carried out in a rotatory evaporator at 20°C in water-pump vacuum.

Pesticide-grade hexane from Fisher Scientific Company was used as received. Pesticide-grade hexane from Matheson Coleman & Bell, supplied by Canlab, was distilled to remove a small amount of a high-boiling fraction, and pesticide-grade benzene (5 ml/l) was added to the distillate to obtain elution patterns identical with those of the Fisher Scientific Company pesticide-grade hexane (Zitko, 1971a). UV spectra of these 2 pesticide-grade hexanes and of pesticide-grade hexane from Mallinckrodt are presented in Appendix. An aliquot of the sample extract (2-20 ml, depending on the expected concentration of PCB and pesticides) was evaporated to a small volume (1-1.5 ml) and applied to the alumina column. The solution was washed into the column with an additional 1.5 ml of hexane and the column was washed with hexane until 20 ml of effluent was collected. The effluent was evaporated to a small volume (1-1.5 ml), applied to the silica column, and washed into the column with 1.5 ml of hexane. The column was washed with hexane, the first 10 ml of the effluent was collected as fraction I, the next 20 ml of the effluent as fraction II. After collecting the fraction II, the eluting solvent was changed to a 10% solution of diethyl ether in hexane and 10 ml of this effluent was collected as fraction III.

The fractions were evaporated to dryness, the residue was dissolved in a known volume of hexane (0.2-30 ml, depending on the concentration of PCB and pesticides) and analysed by gas chromatography. In some cases a contaminant was eluted in fraction III. This impurity appeared as a somewhat unsymmetrical, tailing peak with a retention time similar to that of p,p'-DDE and could be removed by passing fraction III through the alumina column, eluting with hexane and collecting 20 ml of effluent.

A Packard A7901 gas chromatograph with a glass column (6 ft x 4 mm), containing 4% SE-30 on Chromosorb WAW 100-120 mesh, operated at 200°C, was used. Carrier gas was nitrogen at a flow rate of 60 ml/min. Injector and detector were kept at 210°C, D.C. voltage in the electron-capture detector was 90V and the meter sensitivity was 3×10^{-9}A.

Standard solutions of Aroclor 1254, p,p'-DDE, and 2 different mixtures of pesticides were injected daily to calibrate the detector. The concentration of the Aroclor 1254 standard solution was 2.205 µg/ml, that of the p,p'-DDE standard solution was 0.96 µg/ml. Pesticide mixture M-8 contained hexachlorobenzene, aldrin, heptachlor epoxide, p,p'-DDE, p,p'-DDD, and p,p'-DDT in concentrations of 0.0232, 0.160, 0.302, 0.401, 0.455, and 0.450 µg/ml, respectively. Pesticide mixture M-9 contained lindane, heptachlor, heptachlor epoxide, dieldrin, p,p'-DDD, and p,p'-DDT in concentrations of 0.155, 0.155, 0.302, 0.216, 0.455, and 0.450 µg/ml, respectively.

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To eliminate the evaporation of hexane from the standard solutions, the solutions were kept in 6 ml hypovials closed with Viton septa (Pierce Chemical Company).

Several different volumes of the standard solutions were injected to be sure that the detector response is linear in the range used.

The detector response to the chlorinated hydrocarbon pesticides, expressed as disc-integrator area per ng for all pesticides except hexachlorobenzene, where the peak height was used, is given in Table V.

Table V. Electron-capture detector response to chlorinated hydrocarbon pesticides.

Pesticide	Response/ng	Relative response/ng (p,p'-DDE = 1.00)
Hexachlorobenzene	142 ± 4.3*	
Lindane	7.74 ± 0.77	1.15
Heptachlor	8.32 ± 0.77	1.24
Heptachlor epoxide	7.15 ± 0.43	1.07
p,p'-DDE	6.70 ± 0.37	1.00
Dieldrin	7.04 ± 0.32	1.05
p,p'-DDD	4.96 ± 0.04	0.74
p,p'-DDT	4.56 ± 0.16	0.67

*Standard deviation

Two different electron-capture detectors were used in the present study. Detector A was in operation from January 1971 until March 1971. Detector B was used from June 1971. The long-term changes in the responses of the detectors to p,p'-DDE and Aroclor 1254 are presented in Table VI. Peak area was used in the case of the detector A, peak height in the case of the detector B so that the results are not comparable in the actual response value, but they are comparable from the point of view of long-term changes. The increasing response of the detector B was not due to changes of the standard solutions on standing. Fresh standard solutions injected on the 50th day gave responses of 8.59 and 3.73 for p,p'-DDE and Aroclor 1254, respectively. It is likely that the long-term trend in the detector response is caused by the conditioning of the column, as a result of which larger amounts of injected compounds reach the detector. With the electron-capture detector alone, it is impossible to measure the amount of the injected compound actually reaching the detector.

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Table VI. Long-term changes of the electron-capture detector response.

Day	Response to p,p'-DDE		Response to Aroclor 1254
	Detector A	Detector B	Detector B
1	5.77	4.37	1.59
2		4.29	1.40
3		4.28	1.43
4		4.87	1.51
5	5.42	4.18	1.68
7	6.24		
8	6.25	6.22	2.36
9		5.60	2.39
10		5.77	2.42
11		5.49	2.69
12	5.41		2.35
13	5.19		
14	6.61		
15	5.83	5.96	2.68
16	4.90	6.03	2.60
17		6.02	2.77
18		6.54	2.78
19	5.36	5.91	2.78
20	5.08		
22	5.28	6.45	2.82
23	5.57	6.39	3.04
24		7.36	3.19
26		6.45	3.03
28	5.25		
29	5.79	7.37	3.26
30		7.48	3.47
33	4.47	7.75	3.47
35	4.91		
36	5.59		
37		7.56	3.39
38		7.44	3.46
39		7.46	3.70
40	3.92	7.84	3.74
41	5.18		
42	6.52		
43	6.60	7.01	3.30
44	5.42		
47	5.55	8.14	4.01
48	5.50		
49	5.22		
50	4.57	7.77	3.89
51	4.60		

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(Table VI. Cont'd)

Day	Response to p,p'-DDE Detector A	Response to p,p'-DDE Detector B	Response to Aroclor 1254 Detector B
55	4.65		
56	4.79		
57	4.61		
58	5.17		
61	5.04		
62	4.54		
63	4.81		

Results of the analysis of 2 pesticide-spiked corn oil samples are presented in Table VII. The sample A was spiked in this laboratory, the sample B is an O.E.C.D. exchange sample for which the identity and concentration of chlorinated hydrocarbon pesticides was not known at the time of the analysis.

Table VII. Analysis of corn oil spiked with chlorinated hydrocarbon pesticides.

Pesticide	Concentration, µg/g Sample A Added	Sample A Found		Sample B Added	Sample B Found
Hexachlorobenzene	0.29	0.23	0.22		
Lindane	1.95	2.26	2.06		
Heptachlor	1.95	2.22	1.85		
Aldrin	2.02	2.24	2.25		
Heptachlor epoxide	3.81	3.51	3.59	4.0	3.32±0.27*
p,p'-DDE	5.09	5.72	5.41	15.0	11.89±1.90
o,p'-DDT				3.5	1.06±0.49
Dieldrin	2.72	2.98	3.16	5.0	3.98±0.61
p,p'-DDD	5.70	4.18	3.99	7.5	5.75±0.68
p,p'-DDT	5.70	6.77	5.59	4.5	3.83±0.97
p,p'-dichlorobenzophenone				2.0	not detected

*Standard deviation

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Average recovery of Aroclor 1254 in the analytical procedure was 105.5%.

PCB were quantified in terms of Aroclor 1254. In some samples the areas under the second, fourth, and sixth major Aroclor 1254 peak (see the gas chromatogram in Appendix) were used. In other samples the quantification was carried out using the total height of the first, second, fourth, fifth, and sixth major Aroclor 1254 peak. The latter method is faster and yields practically identical results as demonstrated in Table VIII.

Table VIII. Comparison of two PCB quantification methods.

	PCB, μg/g	
Sample	Peak height	Peak area
Herring gull eggs	6.92	7.06
Cormorant eggs	41.3	34.4
Black duck eggs	5.05	4.63
Herring	0.43	0.32
Trout exposed to Aroclor in the lab		
Muscle	5.50	6.30
Liver	52.5	57.0
Caeca	208	228

Duplicate extracts were prepared from some samples, particularly from those with high levels of PCB and p,p'-DDE, and each extract was analyzed in duplicate. Results of single analyses are reported for other samples. The precision of the duplicate determinations was reasonably good in terms of residue analysis, the standard deviation being about 6-15%. Standard deviations of the egg analyses are given in Table III, additional data are presented in Table IX.

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Table IX. Precision of PCB, p,p'-DDE, p,p'-DDD, and p,p'-DDT determinations.

Sample	PCB	p,p'-DDE	p,p'-DDD	p,p'-DDT
	μg/g			
Herring	0.41	0.07	0.03	0.10
	0.46	0.09	0.03	0.09
	0.45	0.10	0.02	0.08
	0.41	0.10	0.01	0.06
Mean±Stand.Dev.	0.43±0.026	0.09±0.014	0.02	0.08±0.017
Cormorant (O.E.C.D. exchange sample)	398	14.8	-	traces
	425	16.2	-	"
	443	15.6	-	"
	373	12.2	-	"
	369	12.7	-	"
Mean±Stand.Dev.	402±32	14.3±1.76	-	
Herring gull muscle	5.01	2.13	-	traces
	5.12	1.99	-	"
Atlantic salmon smolt* (whole fish)	about 0.1	0.46	0.72	1.10
	" "	0.49	0.67	1.22
	" "	0.39	0.79	1.42
	" "	0.37	0.69	1.21
Mean±Stand.Dev.		0.42±0.057	0.72±0.053	1.24±0.13
	" "	0.68	0.12	0.06
	" "	1.04	0.18	0.07
	" "	0.41	0.39	0.39
	" "	0.38	0.35	0.33
Mean±Stand.Dev.		0.63±0.30	0.26±0.13	0.20±0.19

*Exposed to technical DDT; different fishes were used to obtain duplicate extracts.

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CONCLUSIONS

A variety of halogenated compounds is used in industry and incorporated into numerous products. These compounds enter the environment and may be accumulated in the biomass as already demonstrated in the case of PCB, hexachlorobenzene, byproducts from vinylchloride production, and PCT. PCB and hexachlorobenzene were detected quite easily since they accompany chlorinated hydrocarbon pesticides during the analysis. Modified conditions had to be used to detect low-molecular weight chlorinated hydrocarbons and PCT. It is very likely that other halogenated hydrocarbons will also be detected in the environment as soon as suitable analytical methods become available. Some of the compounds may already now be seen as unidentified peaks in the routine determination of chlorinated hydrocarbon pesticides.

Very little is known about the fate and toxicological significance of industrial halogenated hydrocarbons in the environment. Levels of hexachlorobenzene in livers of some species of birds in The Netherlands are well above those found in birds fed on a diet containing hexachlorobenzene at the no-effect level in the laboratory. No dose-level-effect relationship has been established for PCB.

The rate of accumulation of PCB and hexachlorobenzene in the environment is not known, since the levels have not been monitored for an extended period of time. It is possible that a steady-state situation exists in some areas. The world consumption of industrial halogenated hydrocarbons should be determined. This together with some toxicity data already available and some extrapolations would determine research priorities. Until more refined data on acceptable levels of halogenated hydrocarbons in the environment become available, these compounds should be considered potentially harmful and their discharge into the environment should be limited as much as possible.

In studies of sublethal effects of PCB on fish and other aquatic animals, great care should be taken to secure uncontaminated controls, mainly by using a PCB-free diet.

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ADDENDUM

Additional information was obtained while this report was in typing.

PCB were characterized by gas chromatography on SE-30 support-coated open capillary columns. ^{36}Cl-labelled Aroclors 1248 and 1254 were prepared by neutron irradiation (Stalling et al., 1971), and the preparation of ^{3}H-labelled PCB by selective labelling and nonselective chlorination in the gas phase over ferric chloride was described (Igekami et al., 1971). In addition to chlorinated paraffins and PCB, sheet materials may be fireproofed by pentabromotoluene, tetrabromobenzene, trichlorotribromobenzene, decabromobiphenyl, chlorinated rubber, brominated soybean oil, and perchloropentacyclodecane. Chlorinated paraffins are used for cotton, paper, and unbleached kraft based boxboard and corrugated medium. Adhesive compositions for laminates may, in addition to chlorinated paraffins, contain PCB of the 54 and 60% varieties (Thiery, 1971).

Flame retardant compositions for polyolefins, poly (oxymethylene), nylon, and cellulose acetate are based on chlorinated hydrocarbons with boiling point above 200°C, containing more than 40% chlorine, and phosphinic acid derivaties. Hydrocarbons frequently mentioned in this report, and hexachlorobenzene, 2,3,5,6-tetrachloro-p-xylene, and α,α-dichloro-m-xylene can be used (Cannelongo, 1971).

Chlorinated paraffins Cereclor 42 and Cereclor 70 are used in high-build marine primers (Bowerman, 1971).

Fire retardants based on polyhalo polyhydro polycyclic dicarboxylic acid imides were patented (Cyba, 1971).

TCDD, administered orally to pregnant rats on days 6-15 of gestation, had no effect on foetuses at the 0.03 µg/kg day level and foetal mortalities were observed at and above 0.125 µg/kg day. Decrease of maternal weight gain started at 0.5 µg/kg day and a severe toxicity was evident at 8.0 µg/kg day (Sparschu et al., 1971). Hexachlorobenzene is neurotoxic in male rats (Lehotzky et al., 1971).

Current U.S. maximum acceptable levels of PCB in eggs, and ready-to-eat poultry and pork are 0.5 and 5 ppm, respectively (Anon., 1971a,b).

PCB contaminated fish meal, feed, eggs, and chickens were very recently found in the U.S.A. Fish meal imported from Peru contained 6.7-7.3 ppm of PCB. Meat scrap meal at an Illinois plant contained PCB at 1 ppm. The range of PCB found in total edible tissues is 0-5.3 ppm in hens, 0-0.7 ppm in broilers, and 0-11.8 ppm in turkeys (Anon., 1971b). It is not clear at the moment how much of this contamination is caused by industrial accidents (PCB leakage

from heat-transfer systems) and what is the contribution of the environmental levels of PCB.

The concentration of PCB and chlorinated hydrocarbon pesticides was determined in a few additional samples and the results are presented in Table X.

Table X. Additional data on PCB and chlorinated hydrocarbon pesticides in aquatic animals.

Species	Location	PCB µg/g	p,p'-DDE µg/g	Other
Basking shark *Cetorhinus maximus* (Gunnerus)	Eastern Canada			
(muscle)		0.06	traces	
(liver)		1.37	"	
(muscle)		0.07	"	
(liver)		0.77		
White shark *Carcharodon carcharias* (Linnaeus)	Leopardville, N.B.			
(muscle around backbone)		0.64	0.57	
(" " pect. fin)		0.77	0.48	
(liver)		218	335	DDT 63, DDD 43
Bluefin tuna *Thunnus thynnus*	Eastern Canada			
(muscle)		1.54	0.15	
Atl. ribbed mussel *Volsella demissa*	Miramichi estuary, N.B.	0.09	0.01	
Clam *Mya arenaria*	Bathurst, N. B.	0.09	traces	

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Sea Sense

PCB TIME BOMB

A new and dangerous "ecological time bomb" threatens the aquatic environment. It menaces some of the nation's great commercial and sport fisheries. It has caused skin disease, reproductive failure and neurological disorders in human beings. During laboratory tests it has sparked a form of cancer in small animals.

It is polychlorinated biphenyl (PCB) pollution. Apart from DDT it is the most ubiquitous synthetic pollutant in the biosphere.

Wildlife from New England to the Great Lakes and part of the Pacific coast are tainted by significant PCB contamination. Measurable levels of this long-lasting industrial chemical can now be found in half the population of the United States. PCBs were first detected in 1966 by the Swedish scientist Soren Jensen who discovered traces of it in pike and, later, in the hair of his entire family. However, only a fraction of the PCBs, produced domestically since 1929, is causing this crisis. Most of the chemical is either still in use, locked in landfills or lurking in the bottom mud of lakes and waterways.

Now used primarily in sealed electrical components, PCBs are valued as an insulating medium which will not burst into flame at high operating temperatures. As such, it has been used in up to 95 percent of all capacitors and five percent of the transformers manufactured in the United States. PCB parts are currently found in such common household appliances as air conditioners and fluorescent light fixtures. It is also used in certain marine caulking compounds and investment casting waxes.

This extreme stability is an attractive feature for industries and the characteristic which makes PCBs an environmental time bomb. Once released into the environment, PCBs last for decades. Slowly the chemical rises along the food chain until contamination concentrations are massed in fish and predators which eat the fish. Incineration at temperatures exceeding 2,400°F is the only known disposal method for this tough toxic substance.

Faced with this hazard, electrical industry officials have agreed to stop using PCBs as soon as an "acceptable substitute" is available. The Monsanto Chemical Corporation, sole American manufacturer of the compound, has already agreed to phase out PCB production as new insulating fluids are developed. Five years ago this company voluntarily restricted PCB sales to "closed systems" such as electrical parts.

Switching to a new insulating fluid will not, however, end the PCB problem. Prior to 1971 this chemical was poured into a wide range of consumer products. Carbonless carbon paper, paints, textiles, hydraulic fluids and sealants often contained PCBs. Buried in landfills with decaying electrical machinery, these materials are believed to be a significant source of pollution.

Imports, which topped 300,000 pounds in 1974 alone, and direct PCB discharges from industry are two additional contamination sources.

PCB contamination in wildlife and man is measured in much smaller terms — usually parts-per-million. Low levels of this powerful pollutant are magnified by the natural process of bioaccumulation. Through this process, PCBs are concentrated in animal tissues at levels up to 40,000 times greater than those in the surrounding environment. Bioaccumulation can also account for a single factory fouling a major river system.

When released into the environment, PCBs wash into waterways where the

Once released into the environment, PCBs last for decades.

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Incineration at temperatures exceeding 2,400°F is the only known disposal method for this tough toxic substance.

contaminant settles to the bottom of the pond, stream or harbor. It is basically nonsoluble in water but is able to enter small marine life.

Owing to its insolubility in water, PCBs tend to accumulate in the fatty tissues of fish and other animals. As each predator eats a smaller organism it absorbs and retains the PCBs present in the smaller or weaker animal. By the time an osprey, gull or man feeds on the fish, PCB levels, which cannot readily be detected in the water, can have bioaccumulated to significant readings.

One of the first signs of growing PCB pollution came through nature's own early warning system – contamination of wildlife. Since 1970, pesticide monitoring by the United States Fish and Wildlife Service has reflected a deterioration of environmental quality.

Exceedingly high levels of PCBs are now found in fish from the Hudson River in New York; the entire Great Lakes system; New England's Merrimac and Connecticut Rivers; the Mississippi, Missouri and Ohio Rivers in the midwest; the northwest's Columbia River system; the Sacramento River in the west; the Rio Grande and other Gulf Coast streams; the Yukon River in Alaska and the waters of the Los Angeles bight.

"The omnipresence of PCB residues in our environment looms as a very dark cloud casting an ominous shadow upon all our fish and wildlife resources programs which depend on environmental quality and healthy habitats," said Assistant Secretary of the Interior Nathaniel P. Reed. "In particular, PCBs pose an immediate threat to our efforts to preserve and protect threatened and endangered species.

"Under present conditions, PCBs may very well pull the rug out from beneath us by destroying marginal species in spite of our best efforts for preservation," Reed warned.

Government efforts to restore the Atlantic salmon in the northeast as well as restoration of the Great Lakes fisheries – a seventeen-year project with a $33 million price tag – are jeopardized by this pollutant. Large lake trout and salmon from Lake Michigan have repeatedly surpassed maximum PCB limits for safe human consumption. Contamination of commercial species is also present in carp, chubs, smelt and alewives taken from this area, Reed affirmed.

Should the United States Food and Drug Administration cut its PCB maximum from 5 to 1 or 2 ppm, then virtually all species would be restricted and the entire Great Lakes fishery would be curtailed. These fisheries have an annual dockside value of $19 million and contribute some $95 million a year to the economies of Canada and the United States when processing, shipping and retailing are considered.

"Nothing short of immediate drastic action will enable us to raise anything better than lakes full of eunuchized fish," the assistant interior secretary said. "With the present preponderance of PCBs, the life span of Great Lakes fishery will be limited to a single generation.

PCBs are concentrated in animal tissues at levels up to 40,000 times greater than those in the surrounding environment.

"We must immediately respond to the dangers posed by PCBs. They represent an ubiquitous degenerate influence on our national health and well being."

A 1968 incident in Japan revealed the clear – and tragic – impact of this chemical on human health. For several months more than 1,000 unsuspecting people consumed rice oil accidentally laden with up to 2,000 ppm PCB.

Stillbirths, miscarriages, visual impairment, skin disease, neurological disorders, hearing loss, discharge of a cheese-like substance from the eyes, swelling of the eyelids, systemic gastrointestinal symptoms with jaundice – these were the primary symptoms manifested by Japanese victims. Scientists now call this disease the "Yusho syndrome."

"In some patients, symptoms persisted for three years after PCB exposure was discontinued," a background report on the incident by the National Institute for Occupational Safety states.

"Infants born to poisoned mothers had decreased birth weights and showed skin discoloration due to PCB placental passage," it continued.

Authorities say the contamination began when heat transfer pipes immersed in the oil during processing developed pin-size holes which allowed PCBs to mix with the product. Most patients suffering from the Yusho syndrome recovered very slowly, suggesting that the toxic compound remains in the body for a long time after it is first ingested.

But the full effect of this mishap cannot be gauged in scientific terms or measured in parts-per-million.

Kamino Rioko was twenty-eight years old when the poison struck. Skin lesions covered her body. Long after her exposure to the PCB-laden rice oil, Ms. Rioko suffered from nausea, a low-grade fever and monthly swelling of her face and le-

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sions. She still carries the scars of PCB poisoning.

"After I was stricken, I began to envy my friends who have babies to take care of," Ms. Rioko said in a recent television interview. "Thinking of those happy women, I felt lonely and desperate.

"If I get married and my husband lets me have babies, they might be stricken too. That would be too much of a burden for my husband. So, if someone proposes to me, I won't accept. I can't marry unless I am completely cured.

"A number of my friends are married. They have one or two children already. Sometimes I visit them, but when I do, their children ask me, 'What happened to you? How did you get holes in your face?' Children are shocked when they see me. Children are honest and to them what's ugly is ugly."

Although PCB concentrations in this rice oil were unusually high, data on the incident was the best toxicological information available to the United States Food and Drug Administration (FDA) officials for establishing a limit for the compound in American foods. Some FDA scientists say use of this data led the agency to underestimate the effect of low-level PCB doses on human health. New studies suggest ingestion of this chemical at levels well below federal maximum tolerances may be harmful.

Factory workers in plants manufacturing PCB-filled capacitors and transformers have been exposed to this toxic substance at close quarters for long periods. As might be expected, the effects on health attributable to this compound have been studied by the industry and medical officials at agencies such as the National Institute for Occupational Safety and Health (NIOSH).

A NIOSH report on this compound states that "The known effects of PCBs in humans include an acne-like (skin) eruption – chloracne – pigmentation of the skin and nails, excessive eye discharge and distinctive hair follicles." "For a number of years, chloracne of the face and neck have been reported among workers exposed to chlorinated hydrocarbons (a chemical classification which includes PCBs)."

Other symptoms cited after PCB exposure include digestive disturbances, edema of the face and hands, burning of the eyes, impotence and hematuria.

"It's just like you have water blisters underneath the skin, and there's a lot of pussy blood," one man explained after working in a factory with PCBs for several years. Working with PCBs made one's hands sore. The skin would crack open and the fingers hurt. Gloves were needed to perform simple tasks. Two or three times a day the gloves had to be changed. They were full of blood and pus.

The long-term effects of PCBs may not be easily controlled. Recent experiments imply that the compound can, even at low levels, wreak havoc on the health of laboratory animals.

At the University of Wisconsin Medical School, Dr. James Allen is probing the impact of PCB doses at and below the current FDA "safe limit."

Despite concentrations of only 2.5 and 5 ppm, Rhesus monkeys used in the tests had stillbirths and miscarriages and suffered skin lesions and hair loss. Allen's findings suggest an inverse relationship between PCB exposure and successful reproduction. After three matings with males, 12.5 percent of the monkeys exposed to 5 ppm PCB feed became pregnant. Three matings led to pregnancy among 37.5 percent of the animals eating 2.5 ppm PCB food. But in the control group – which did not consume any PCBs – 90 percent became pregnant after three attempts.

Other similarities between test results and the Yusho syndrome surfaced in Allen's findings. Young born to PCB-infected mothers were smaller than normal baby monkeys. Because the reproductive system of the rhesus is similar to that of humans, this monkey is often used in medical experiments. Yet Allen and other researchers agree that current experimental data cannot be applied directly to man. Perhaps the most disturbing

Under present conditions, PCBs may pull the rug out from beneath us by destroying marginal species in spite of our best efforts for preservation.

part of the new research being conducted is a study suggesting that PCBs can cause a form of liver cancer in some animals. Reported by Dr. Renate Kimbrough, of the United States Center for Disease Control in Atlanta, 184 female rats were used in the experiment. After ingesting food tainted with 100 ppm PCB for twenty-one months, twenty-six of the 184 rats had developed malignant liver tumors. Only one of the 146 control animals developed this disease. Of the 184 rats in the PCB group, 146 developed tumorous liver lesions.

Faced with this kind of data and increasing signs of continued PCB contamination in wildlife, Canada imposed, last fall, a new PCB limit in human foods. Set at 2 ppm, Canada's limit is less than half the United States tolerance.

FDA officials are now in the midst of

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reviewing the American standard. Some admit there is little scientific basis for the current 5 ppm PCB figure. According to Staff Scientist A. Karim Ahmed, the Natural Resources Defense Council (NRDC) has petitioned FDA to set a new limit of zero for PCB contamination in human foods.

But, Dr. Ahmed admitted, the stricter the standard, the more severe the impact on sport and commercial fishing. Setting a limit close to zero – or even one or two ppm – would close some of the country's greatest fishing resources. It may take decades for natural purification of these fisheries. Until then the only way for many people to control their PCB intake may be to eat less fish.

PCBs are a global form of pollution. Though centered in urban areas, PCB pollution extends to the Chesapeake Bay, Puget Sound, the Hudson River and the San Francisco Bay.

The range of wildlife affected by this potent pollutant includes one of America's favorite waterfowl – the canvasback duck. The canvasback likes to feed on small snails which absorb high levels of PCBs and are susceptible to other forms of contamination. Survival of the duck may be determined by the fate of these snails and their ability to stay alive despite the contamination of the environment.

Dr. Donald White, of the Patuxent Wildlife Research Center in Laurel, Maryland, reported that the duck wings from Massachusetts, Rhode Island, New York and Connecticut were the most contaminated of the samples taken from the fourteen Atlantic coast states tested. He found that some composite samples of wings registered twice the FDA limit for poultry.

Unfortunately, many Hudson River fish have been hit harder by PCBs than the fowl of the Atlantic flyway. Striped bass, rock bass, large-mouth bass, shiners, smallmouth bass, northern pike, sturgeon and white perch in this waterway all bear the mark of the chemical.

This pollution has closed a $1.25 million commercial striped bass fishery in the Hudson and endangered an even larger sphere of sport fishing. Owing to the migratory movements of striped bass, some scientists fear the contamination may spread to populations caught in Chesapeake Bay, Long Island Sound and the Delaware River.

PCBs in the Hudson appear to be concentrated near two General Electric (GE) factories in the Fort Edward-Hudson Falls area north of Albany. Environmental groups charge that the plants have dumped up to thirty pounds of the chemical per day into the river. Capacitors insulated with PCBs are produced in the two GE plants.

Composite values for fish caught near one GE facility registered typical readings near 20 ppm during New York State tests. The concentration of the chemical in an American eel exceeded 400 ppm. The PCB levels in striped bass caught near Albany ranged from twice the FDA limit to 89.76 ppm. Near West Point – some fifty miles above New York City – readings from striped bass ranged between 1.17 and 7.54 ppm. An American shad, taken near Poughkeepsie, registered 9 ppm PCB.

Based on this kind of data, Ogden Reid, then commissioner of New York's Department of Environmental Conservation, warned the public against eating striped bass from the river. Reid's move, according to some ecologists, ended a state cover-up of the problem. His action also began the current interest in PCB pollution and led to a series of state hearings on General Electric's discharges.

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The first set of state hearings ended with a preliminary finding that GE had violated state laws regulating the discharge of toxic substances into New York waters. The hearing examiner ruled that General Electric had contributed to the Hudson's PCB contamination.

A second series of hearings on possible remedies for the problem have just concluded. One plan for purging PCBs from the waterway focuses on the dredging of bottom mud – where the nonwater-soluble chemical settles and slowly accumulates. This program could cost $30 million, and GE could be ordered to bear part of the expense.

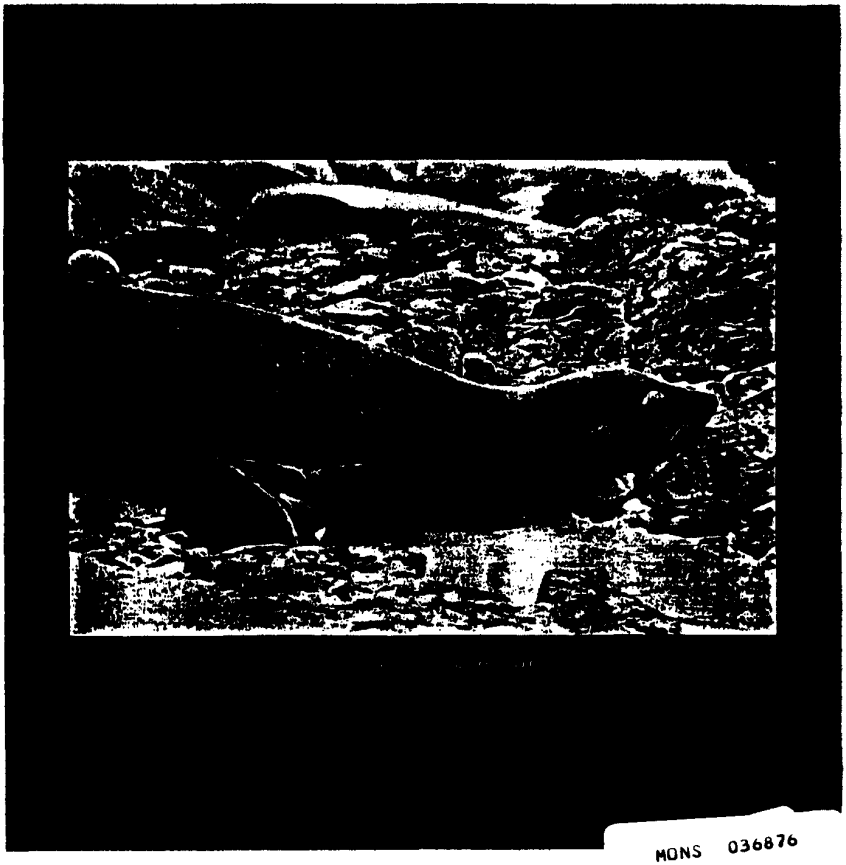
This year, as a result of PCB contamination, New York closed the Hudson to all commercial fishing except for sturgeon, shad and goldfish. Federal scientists estimate it could take decades for an ecosystem, like that of the Hudson, to cleanse itself of this contamination. Sadly, significant PCB contamination of wildlife is not limited to ducks or the Hudson River.

The same United States Environmental Protection Agency (EPA) study reports up to 350 ppm PCB in Hudson fish also includes readings as high as 165 ppm for samples from Lake Michigan. Since 1971 Michigan state authorities have warned against eating salmon or trout from the lake more than twice a week.

Last year 125,000 cans of coho salmon taken from the lake were seized and condemned by federal officials for exceeding FDA PCB limits. An additional 6,480 pounds of frozen coho and chinook salmon from the lake were confiscated for the same reason.

Tests, in 1974, by the Michigan Department of Natural Resources showed PCBs ranging from 10 to almost 25 ppm in Lake Michigan coho salmon and lake trout. Additional studies by the Wisconsin Department of Natural Resources re-

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vealed that this chemical also effected a wide variety of other fish. Readings from lake trout exceeded 40 ppm and from carp surpassed 50 ppm in these tests.

A few months ago, federal officials condemned and buried 20,000 pounds of carp taken from Lake Pepin, part of the Mississippi River downstream from the Twin Cities. Fish from this area contained as high as 40 ppm PCB.

Striped bass caught in the western end of Long Island Sound last fall came within 0.05 ppm of the FDA limit. Five years ago Dr. Robert Risebrough, of the University of California at Berkeley, found significant PCB contamination in fish from this area.

Canadian scientists say the chemical present in smelts and eels from Lake Ontario and eels from the Saint Lawrence Seaway frequently surpasses the country's 2 ppm PCB standard. Along with coho salmon from the Great Lakes, chubs from Lake Huron and lake trout from Lake Superior are also affected.

Although PCB pollution is still a problem, primarily in inland waters, deposits in harbors and along the coasts, particularly near river mouths, are significant. The chemical in fish taken off the coast of Southern California has exceeded the FDA maximum.

Moreover, PCBs have also been found in wildlife and fish from Holland, off the Scottish coast, Germany, the Baltic Sea and Japan during the past decade. They have been detected in marine life ranging from plankton to tuna.

Fish-eating birds have borne the brunt of PCB contamination in the aquatic environment. While studying them on Long Island Sound, Dr. Risebrough found PCB levels between 300 and 1,000 ppm in osprey and cormorants. He also concluded that deformities found in terns on Great Gull Island in the Sound could be caused by contaminants such as PCB compounds.

"Severe reproductive failure has been

PCB pollution has closed a $1.25 million commercial striped bass fishery in the Hudson and endangered an even larger sphere of sport fishing.

identified in herring gull colonies around Lake Ontario," Karl Bremer, of EPA's Chicago office, wrote recently.

"There is a positive correlation between early embryonic mortality and PCB concentration," he concluded. Birds like the osprey and gull suffer most from PCB contamination, for they stand at the top of a complex food chain which magnifies low-level PCB concentration up to 40,000 times in one step.

Research scientists in California found a correlation between high levels of DDT and PCBs in adult sea lions and aborted fetuses. While in 1969 the corpses of 12,000 sea birds washed up on the western coast of Britain showed considerable PCB contamination.

More significant, perhaps, was the discovery of PCBs in practically all specimens collected in a survey of the mid-Atlantic. Affected samples included phytoplankton, zooplankton, sargassum weed, flying fish, dolphins, and sharks. The plankton, in particular, contained about ten times as much in proportion to its weight as the other marine organisms.

After the 1968 rice oil incident, Japan moved quickly to ban PCBs. Now the chemical can neither be used in nor imported to the island nation. EPA Administrator Russell Train accepts United States industry claims that a similar move here would simply switch an environmental for a fire hazard.

Train said the key to controlling PCB contamination here rests with disposal practices for the 300 million pounds of the chemical now in use. Another 200 million pounds of potential contamination are buried in landfills.

At the heart of the PCB problem is the EPA's lack of jurisdiction. Until Congress approves a Toxic Substances Control Act, the agency is powerless to deal with non-pesticides in use or some of the 600 new chemicals introduced annually.

"PCBs are a significant hazard to human health and the environment," Train told a congressional subcommittee this year. "However, the PCB problem is but one dimension of a much larger picture of environmental degradation by toxic chemicals. We have no authority to control (non-pesticides) uses and must rely on the Federal Water Pollution Control Act and Clean Air Act to achieve pollution control."

Without additional protection, America will continue to use its citizens, fish and wildlife resources to learn what the nation's environmental problems are.

The only prospect on the horizon for control of this pervasive pollutant comes from the work of Dr. Dickson Liu at Canada's Center for Inland Waters in Burlington, Ontario. Dr. Liu found that a variety of common bacteria often present in sewage can reduce PCB concentrations from 300,000 to 20 parts-per-billion. The chemical is broken down into harmless carbon dioxide gas and lightweight organic acids normally found in nature. There is some question whether this process can be applied to large scale industrial polluters or in clean-up drives. A pilot plant testing Dr. Liu's theory is scheduled to open this summer in Canada.

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