RATES AND ROUTES OF TRANSPORT OF PCBs IN THE ENVIRONMENT

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

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

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

PRODUCTION AND USE IN NORTH AMERICA

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

according to category of use and grade of Aroclor.

Prior to Monsanto's voluntary reduction of sales in September, 1970, approximately 60 percent of sales were for closed-system electrical and heat transfer uses, 25 percent for plasticizer applications, 10 percent for hydraulic fluids and lubricants, and less than 5 percent for miscellaneous applications such as surface coatings, adhesives, printing inks, and pesticide extenders. Exports by Monsanto have averaged 13 percent of domestic sales over the period 1963 to 1970. Imports are thought to be small comprising primarily of plasticizers in resins and adhesives, transformer oils and capacitor fluid in electrical equipment. Exports to Canada should be of the order of 7 percent of U.S. sales and are included in this model of North America. Monsanto has restricted sales of Aroclors based on consideration of either the possibility of contamination of food products or its inability to control or monitor possible losses into the environment. The fraction of sales for use in confined systems, primarily electrical and heat transfer applications, will increase to approximately 90 percent in 1971. The higher chlorinated Aroclors, 1254 and above, comprised approximately 30 percent of sales piror to 1971. Their share of the reduced sales in 1971 is expected to fall to 22 percent. Aroclor 1242 is being replaced with Aroloclor

1016 having a similar composition but with isomers containing 5 or more chlorine atoms removed.

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

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

ROUTES INTO THE ENVIRONMENT

As in the case of most industrial chemicals, loss figures for PCBs are practically non-existent. Possible routes into

the environment include: (1) leaks from sealed transformers and heat exchangers; (2) leaks of PCB-containing fluids from hydraulic systems which are only partially sealed; (3) spills and losses in the manufacturing either of PCBs or PCB-containing fluids; (4) vaporization or leaching from PCB-containing formulations; (5) disposal of waste PCBs or PCB-containing fluids.

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

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

QUANTITATIVE ESTIMATES OF RATES OF LOSS INTO THE ENVIRONMENT

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

Estimates of the rates of loss and disposal of Aroclors in 1970 will be based on rough guesses of the useful service life in different applications. Transformers are fairly permanent

installations, and it is therefore estimated that only 10 percent of sales of transformer fluid is to replace oil that was scrapped and that the remaining 90 percent is for new units. The useful life of capacitors, especially those used in small items such as fluorescent light ballasts, is expected to be under a decade and it is therefore estimated that the rate at which the capacitors are discarded, primarily into landfill dumps, is equal to half the rate of production. (Figure 1 indicates a doubling period for sales of about 10 years.) A similar figure is assumed for the scrapping of heat exchangers, but it is expected that the replacement of fluid decomposed under extreme thermal conditions would have led in the past to additional direct losses, primarily into sewers. It is estimated that the rate of vaporization of plasticizer amounts to 10 to 20 percent of sales (12). Since many plastic objects have relatively short useful lives the rate of disposal of plasticizers into dumps is assumed to equal the residual 80 to 90 percent of sales. Hydraulic fluids and lubricants are rarely reused and it is therefore assumed that a major fraction of these fluids used for this purpose, together with those going into the miscellaneous applications, were scrapped at rates approximately equal to those of corresponding sales.

On the basis of these gross estimates, it appears that only about 20 percent of the 1970 sales in North America, some 7×10^3 tons, represented net increase in the amount of PCBs in service, in transformers, heat exchangers and capacitors. The remainder is assumed to have been discharged into the environment, $1\text{-}2 \times 10^3$ tons by evaporation of plasticizers; $4\text{-}5 \times 10^3$ tons by

leaks and disposal of hydraulic fluid and lubricant plus small amounts by disposal of heat transfer and transformer oils, and 22×10^3 tons by disposal in incinerators, dumps and sanitary landfills. Of the latter, we estimate (13) that 10 to 20 percent (3×10^3 tons) were destroyed by burning, and 2 percent (4×10^2 tons) were vaporized, mainly by open burning of dumps, wire scrap, and auto components (see Table 2).

ROUTES INTO THE ENVIRONMENT

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

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

RATES OF TRANSPORT WITHIN THE ENVIRONMENT

The modes of transport of the PCBs within the environment are complex. Vaporized PCBs will be partially adsorbed on particulate, transported with the prevailing winds, and deposited on land or water by particle sedimentation or rain out. PCBs introduced into water streams may be adsorbed by the waterborne particulates or the benthos; the adsorbed PCBs will diffuse into the bottom sediment, redisolve in the water stream or be entrained with sediment eroded from the bottom surface. The problem is further complicated by the assimilation, transport and degradation of PCBs by the biota. A major fraction of the PCBs discarded in dumps is encapsulated in sealed containers or plastic resins. The rate of loss from these will therefore be low until the confining material is degraded and the PCBs released. The PCBs will then slowly diffuse through the surrounding soil. In principle, the rates of transport may be calculated from knowledge of the physico-chemical properties of the PCBs and the pertinent data on atmospheric conditions, particulate transport, hydraulic dispersion, bottom sediment transport, and biological degradation rates. At present, the data are too incomplete and the interactions between the different elements in the environment too complex to attempt a formulation of but the crudest of

transport models. The similarity between the properties of the PCBs and DDT, summarized in Table 1, permits rough estimation of some of the otherwise unknown routes and rates of transport of PCB from the corresponding information on DDT. In Fig. 4, a generalized model for the distribution and transport of the PCBs is outlined, without any indication of the transport down spatial gradients within the different compartments of the environment. An attempt is made in the following sections to estimate fluxes between and within each compartment.

Air Transport

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

within 2 or 3 days, mostly onto the land mass and coastal waters surrounding urban areas. The small amounts of PCB attached to fine particulates will reside in the atmosphere for extended periods and be transported to remote areas.

Based on the above assumptions, the rate of next input of PCBs by aerial fallout in North America will be a little less than the rate of vaporization, about 1000 to 2000 tons/year. The vapor pressure of Aroclor 1254, the dominant airborne contaminant, is close to that of DDE (21) and it is estimated, by analogy to DDE (17), that the likely half-life of PCB in soil is of the order of five years. The PCBs removed from the soil will become adsorbed to particulates, mostly of relatively short range, and be redeposited and vaporized one or more times until they reach the coast. By analogy to DDE (1,2), the redistribution of PCB by this mechanism is expected to result in the redeposition into the ocean of one quarter of the PCBs that originally fall out in the terrestial environment. The deposition pattern will be influenced by the size distribution of particles to which the PCBs are attached with a major fraction ending in coastal waters and a small amount being transported into remote regions.

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

will be too low.

Water Transport

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

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

over a year suggesting that the PCB's are strongly adsorbed to sediment.

The amounts of PCBs transported to the ocean in solution or suspension in river water isestimated as 200 tons/year (49), a small amount compared to the estimated input into rivers. Irrigation waters amount to about 1/15 of the total river flow and are expected to carry a correspondingly lower amount, about 15 tons/year, of PCB to the terrestial environment.

Dredging and dumping

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

Biota flux

The total quantity of PCBs stored in migratory animals is very small (see below) and their movements cannot account for a significant fraction of environmental transfer of PCBs. The movements with the greatest local significance are probably the migrations of seabirds from the northern to the southern hemis-

phere: these might account for the movement of about a ton per year (28). Human fishing is estimated to remove only 1-2 tons/year from the eastern North Pacific, the western North Atlantic and the Great Lakes (30).

SEPARATION OF PCB ISOMERS IN THE ENVIRONMENT

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

Fractionation

In general, the water solubilities and vapor pressures of PCB isomers decrease with increasing chlorine content, although the decreases are not uniform (Table 1, 31). Hence the processes of evaporation, co-distillation and dissolution in water are expected to fractionate mixtures of PCBs, the lower isomers being much more mobile. This has been confirmed for co-distillation by the results of Freed (21, Table 3), which show that after 60 minutes' steam heating the ratio of the first to the sixth of the seven major chromatographic fractions of Aroclor 1254 was reduced by a factor of 5. Thus environmental transport mechanisms involving these processes are expected to reduce the proportions of the lower isomers in environmental samples near to the point of release, and to augment them in samples from remoter areas.

Photolysis and chemical decomposition

Photolytic decomposition of certain PCB isomers has been reported by Risebrough et al. (32, 33), and Safe and Hutzinger (34, 35). The results of the latter suggest that in natural sunlight some higher isomers are more easily broken down than

the lower isomers (35). Hence photolysis, is expected to reduce the proportions of at least some of the higher isomers. Photolytic dechlorination is also expected to give rise to lower isomers, including some which may not be present in commercial mixtures (35).

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

Metabolism and excretion

Published studies of the dynamics of PCBs in rats and birds (36-39) indicate that the lower isomers are generally taken up and/or retained more efficiently. In each case the proportions of pentachloro- and lower isomers found in the animals' tissues were generally lower than those in the Aroclor mixture to which they had been exposed, but there appears to have been little differentiation of the higher isomers except for one hexachloro-isomer (36-38). It is not clear in each case whether the deficiencies of the lower isomers resulted from metabolism or differential excretion, but it is likely that both occurred. Because of their higher solubility in water (see above), the lower isomers would be expected to be excreted more easily than the higher isomers. In one study on rats, loss of PCBs from the body was markedly retarded by administration of carbon

tetrachloride (36), suggesting interference with metabolism in the liver. In another study with rats, isomers hexachloro-isomers were found in disproportionate amounts in the urine (37). suggesting that the tetra- and pentachloro-isomers were metabolized and the hexachloro-isomers excreted in part, while the heptachloro-isomers were differentially retained. Two studies of metabolism of PCBs in fish (40,41) gave inconsistent results, but showed no marked tendency for the higher isomers to accumulate differentially.

Evidence from environmental samples

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

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

substantial quantities of Aroclors 1242 and 1248 must have been released into the environment (see above), these observations suggest that a large proportion of the lower isomers (those with 4 or fewer chlorine atoms) is missing from the animal samples. However, few critical data have been published. In one set of data from sewage sludge (45, Table 4), none of the lower isomers is clearly deficient. In published chromatograms for birds (38, 46, 47, Table 5) only the lowest isomers (tetachlorobiphenyls) and one higher isomer were markedly reduced in comparison to Aroclor 1254. In human adipose tissue (48), however, pentachloro- and hexachloro-isomers were reduced or missing.

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

The lack of the lower isomers in samples from relatively contaminated areas could be accounted for either by metabolism or by their greater mobility. However, Risebrough & Berger (33) found that lower isomers were relatively deficient also

in samples from fish in a remote lake in northern Canada. This suggests that differential metabolism is the primary mechanism in the environmental differentiation of isomers, outweighing the effects of differential photolysis and differential mobility, which would be expected to have reduced the proportion of higher isomers in remote samples.

Conclusions and comments

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

The above discussion has been confined to a general comparison of lower and higher isomers, because of the scanty published data on relative proportions of isomers in environmental samples. In fact, the physical and chemical properties and biodegradability of PCB isomers are not only a function of chlorine content. More precise data on the exact quantities of individual isomers would permit more precise conclusions about the sources and routes of contamination. We urge that numerical characterization of individual peaks should be published whenever possible.

CUMULATIVE INPUT INTO THE ENVIRONMENT

From an extrapolation of the sales curve in Fig. 1 to zero production in 1930 it is estimated that the cumulative

sales in North America over the period 1930-1970 were 12 to 15 times the 1970 figure, or about 5×10^5 tons. Assuming that the proportions of sales for different uses were similar throughout the period, the cumulative losses may be estimated as about 3×10^4 tons into the air, 6×10^4 tons into fresh and coastal waters, and 3×10^5 tons into dumps and landfills. Using the results of the previous section, it may be estimated that roughly one-third of the PCBs released into the air and one-half of those released into water have now been degraded. It is difficult to estimate the extent of degradation in dumps, because some of the PCBs there may still be in sealed containers, but we assume in any case that leaching from dumps into fresh waters has so far been negligible.

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

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PCB LEVELS AND ΣDDT/PCB RATIOS IN THE ENVIRONMENT

In this section we compare the above estimates of cumulative input into the environment with measurements of PCB levels in physical and biological samples. The purposes of this comparison are: (1) to use the observed distribution of PCBs in the environment to check the consistency of our models of environmental transport; (2) to define the types and locations of input to the environment which are responsible for the most serious contamination of the biota.

Uptake and biological magnification of PCBs in food chains

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

ΣDDT/PCB ratios

Another approach (32,56) utilizes the similarity in properties between the persistent PCBs and the persistent metabolites of DDT, primarily DDE. (In the remainder of this section, DDT and its metabolites DDE and DDD are grouped together as ΣDDT). Experiments suggest that PCBs and ΣDDT are accumulated by aquatic animals to an extremely similar degree from ambient water (41), and measurements in the same areas indicate that the ratios ΣDDT/PCB are very similar in animals from different levels in the food chain (Tables 6 and 7, 32, 56). Hence the ratio ΣDDT/PCB in environmental samples, even in animals at the top of food chains, can be used to infer the ratio in the substrate (22,56). Then the extensive information about the environmental distribution and transport of ΣDDT (2,12) can be used to make inferences about the distribution and transport of PCBs.

Air

The only numerical measurements available of PCB levels in air are some estimates of levels in total suspended particulates (TSP) in four U.S. cities between 1968 and 1970 (E.P.A., unpublished data). The mean level of PCBs was about 50 ppm, with levels in one city substantially higher. This is at least consistent with our earlier estimate based on rates of transport in the environment.

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

Land

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

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

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

In human food, market basket surveys in the United States suggest a ΣDDT/PCB ratio of about 4 (68). Ratios in human milk (69, 70) and human blood plasma (71) are in the same range. However, except for sporadic instances of contamination, most of the human intake of PCBs appears to be in fish (68), whereas ΣDDT is much more widely distributed in the diet (72). If the

fish and shellfish portions of the diet are excluded, the ΣDDT/PCB ratio would probably be greater than 10. Similar data have been reported from Sweden, where the ΣDDT/PCB ratio in total diet samples and in human milk is about 7 (73).

Fresh waters

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

Based on our assumptions of mean concentrations in fresh waters (50), we estimate that the water of the Great Lakes contains a quantity of PCBs of the order of 100 tons; the total quantity in other lakes would be negligible. The quantity carried in river water would be only of the order of 3 tons. It is difficult to estimate the total quantity in the biota, but since the Great Lakes fisheries probably remove less than a ton of PCBs per year (30), the total quantity in fish is probably only of the order of 10 tons. These quantities are negligible in comparison to the estimated cumulative input of 2×10^4 tons after allowing for degradation. Hence we conclude that almost all the PCBs that have been released into fresh waters are adsorbed onto bottom sediments. There are no data to indicate the rate at which they are being released into water and into the biota or being biodegraded.

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

The sea

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

Available measurements of PCB levels and ΣDDT/PCB ratios, summarized in Table 9, are generally consistent with these predictions, although the pattern is less clear than that in Table 8, in part because of the wide variability between species (cf. Tables 6 and 7). The highest PCB levels and the lowest ΣDDT/PCB ratios have generally been in areas close to industrial activity, At least in the Pacific, PCB level decrease and ΣDDT/PCB ratios increase with increasing distance offshore. Data on marine birds summarized by Keith & Gruchy (29) show that these offshore gradients exist in both the Atlantic and Pacific, and show further that PCB levels in the Atlantic seabirds are 5-10 times higher than those in the same or ecologically equivalent species in the Pacific. The correlation of high PCB levels with

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industrial activity has been demonstrated most clearly in Europe, where it has been observed along the coasts of Sweden (65,81), the Netherlands (38) and Great Britain (82).

The only major discrepancy from this general picture is the observation (57) of extremely low ΣDDT/PCB ratios (of the order of 0.01) in zooplankton over a wide area in the North Atlantic Ocean. ΣDDT/PCB ratios in fish in the same area were of the order of 0.2 to 0.5. It is almost inconceivable that aerial fallout of PCBs could have exceeded that of ΣDDT by such large factors over such a large area: hence to explain the discrepancy it is necessary to assume either selective removal of ΣDDT or a local source of PCBs. A likely local source is dumping or leakage from ships. PCBs introduced into the ocean in this way would frequently be mixed with oil, would tend to mix with surface slicks (83), and hence would be peculiarly subject to uptake by plankton. Further study is necessary to confirm this suggested explanation, or otherwise explain the anomalous low ΣDDT/PCB ratio in the Atlantic Ocean.

Assuming the standing crop of fish in the eastern North Pacific to be of the order of 10^8 tons, and that in the western North Atlantic to be of the order of ~~xxxx~~ 5×10^7 tons (derived from 59), we may estimate the corresponding loads of PCBs to be of the order of 10 and 15 tons respectively. Assuming the standing crop of plankton to be five times larger than that of the fish (1,2), the corresponding load of PCBs might be of the order of 100 tons. In the case of ΣDDT, it has been estimated that the total load in marine plants may be several times larger than

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that in marine animals (2); this may be true for PCBs also, but we know of no measurements to support it. In any case it seems unlikely that more than a few x 10^2 tons of PCBs are stored in the marine biota of the area considered, a very small fraction of the total quantity introduced. This fraction may be significantly greater than the corresponding fraction for ΣDDT (1), because of the extraordinarily high levels of PCBs in the zooplankton.

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

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

SUMMARY AND CONCLUSIONS

According to the estimates made in this paper, the PCBs released into the North American environment in the past are now concentrated in three major compartments in the environment: (a) buried in landfill dumps (roughly 3 x 10^5 tons, without allowing for degradation); (b) attached to sediments in rivers and the Great Lakes (roughly 2 x 10^4 tons); (c) attached to sediments on the continental shelf (roughly 10^4 tons). A further substantial quantity (of the order of 2 x 10^4 tons) has been widely distributed over the land and sea by aerial fallout and by disposal from ships. All the numerical estimates are expected to be valid to order of magnitude only.

Transfer of PCBs within the environment is expected to take place by the following main routes: (a) volatilization, aerial transport on particulates, and fallout; (b) leaching from dumps; (c) sediment transport in rivers and in the shallow sea; (d) sedimentation in the ocean. Uptake and transport by the biota

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is probably a ~~minor~~ quantitatively unimportant route of transfer of PCBs, but is of major biological significance. Virtually no evidence is available on the rate of transport by any of these routes, but is is expected that all are very slow. In particular, PCBs in sediments in rivers and lakes are likely to move downstream and augment those in the shallow sea for a long period into the future.

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

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

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

1. Properties and Rates: Data are needed on the solubilities and vapor pressures of individual isomers; on the partition coefficients between water and sediments, water and fats; on the rate of photochemical decomposition and aerobic and anaerobic biodegradation; diffusion coefficients in sediment.

2. Routes. The magnitude of leaching from dumps and aerial transport of PCBs must be established by direct measurements of concentrations in ground waters, airborne particulates, and rainfall. Data are needed on the magnitude of industrial losses in the past.

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

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

5. Bioaccumulation model. Inasmuch as the period since the first commercial application of PCBs is less than the lifetime of a number of species, including man, and the use and discharge pattern has been variable, there is a need to project the long-range impact of the PCBs on the different elements of the ecosystem. Emphasis should be on coordinated approaches to sampling and modelling rather than a statistical accumulation of data.

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13. Approximately 190×10^6 tons of municipal waste and an equivalent amount of industrial solid waste are disposed of annually in the U.S.A., mostly in dumps. Some 4.7×10^6 tons of industrial solid waste are dumped at sea (51). Of the remainder, 18×10^6 tons are burned in municipal incinerators, 14×10^6 tons in commercial incinerators, and 14×10^6 tons in open-burning dumps (14). Emission of PCBCs from these sources may be gauged indirectly from measurements of the emission of combustible matter and polynuclear aromatics. From measurements reported by A.D. Little (15) and Hein and Engdahl (16) it is estimated that 0.25 percent of solid waste is emitted by municipal incinerators and up to 20 percent by open burning. If it is assumed that the fraction of PCBCs in the organic matter evolved from these sources is equal to the fraction of PCBCs in the solid waste, the rate of emission of PCBCs will be of the order of two tons per year from municipal incinerators and 200 tons/year from open burning dumps. The estimates by Hangebrauck et al. (14) of the rate of emission of benzo(A)pyrene from burning sources is used as a gauge of the severity of the combustion in different units. They obtained emission rates of 0.1 tons/year from municipal incinerators, 4.8 tons/year from open burning, 4.8 tons/year from commercial units, and 5.7 tons/year for the burning of automobile components. The estimate of 200 tons/year of PCBCs from the burning of commercial waste and auto components is based on the relative magnitude of combustible pollutants from these different sources, weighted by the estimate of the fraction of total PCB production disposed of in open dumps. These estimates are highly speculative but are considered sufficient to discount the burning of wastes as the major source of PCB emissions.

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50. Only scattered data on concentrations of PCBs in water have been published. Water entering a Swedish water works contained 0.5 ppt (parts per trillion) (45). Industrial rivers in Maine, Massachusetts, Wisconsin and Japan contained levels ranging from 0.2 to 2.8 ppb (42, 51-53). Measured levels in Green Bay and Milwaukee Harbor, Wisconsin, were in the range 20-70 ppt (42, 52). Other estimates can be derived indirectly from DDT/PCB ratios in aquatic fauna (see text). In Lake Michigan, where DDT levels are of the order of 1-3 ppt (54), DDT/PCB ratios in fish are of the order of 0.4-1 (55). In San Francisco Bay, the DDT/PCB ratio in the biota is 1-2 (32, 56), and the level of DDT in the San Joaquin River, the main input to the bay, is about 100 ppt (32). For the rough calculations of storage and outflow made in this paper, we use these data as a basis to adopt 0.5 ppt as a plausible background level for unpolluted fresh waters, 5 ppt for the Great Lakes, 50 ppt for highly polluted rivers and polluted bays, and 500 ppt for highly polluted rivers.

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Table 1. Comparative Physical Properties of PCB's and DDT

(Ref. 9, 23, 84, 85)

		Aroclor 1242	1248	1254	1260	DDT
Molecular Weight	Range*	154-358	222-358	290-392	324-460	352
	Average	262	288	324	370	352
Chlorine		42	48	54	60	50
Solubility++ in H_2O at 20°C (ppb)		200	100	50	Est. 25	0.7
Vapor pressure++ at 38°C (mm, Hg)		10^{-3}	3.7×10^{-4}	6×10^{-5}	2×10^{-7}	$2 \times 10^{-5+}$
Vapor pressure at 20°C (10^{-7}mm Hg)		10^{-5+}	$7 \times 10^{-5+}$	$1.6 \times 10^{-4+}$		1.5×10^{-7}

* Based on constituents present in amounts of 1 percent or more

++ The high values of the solubilities and vapor pressures of the PCB's are a consequence of the heavy weighting given the lower chlorinated species.

\+ Extrapolated

Table 2. Gross Estimates of Rates of Input and Accumulation of PCB's in North America in 1970.

Category of Input	Rates (tons/year)	PCB Grade
Vaporization of Plasticizers	$1-2 \times 10^3$	Mainly 1248 to 1260
Vaporization during Open-Burning	4×10^2	Mainly 1242
Leaks and Disposal of Industrial Fluids	$4-5 \times 10^3$	1242 to 1260
Destroyed by Incineration and open burning	3×10^3	Mainly 1242
Disposal in Dumps and Landfills	1.8×10^4	1242-1260
Accumulation in Service	7×10^3	1242-1254

Reservoir	Accumulation (tons)	
	PCB	DDT
Soil (excluding dumps)	1.5×10^4	3×10^5
Oceans (adjacent to North America)	1.5×10^4	10^5
Fresh Water (dissolved or in suspension)	10^2	$\sim 10^2$
Fresh Water Sediment	2×10^4	?
Biota	$< 10^3$	$< 10^3$

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

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

Table 4. Relative Peak Heights in Gas-liquid Chromatograms of Extracts from Sewage Sludges. [From CaP, 45]

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

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

Peak No.	Relative Retention Time*	Eagle Carcass	Aroclor 1254
1	0.39	7.5	6.8
2	0.49	34.8	100.0
3	0.53	55.0	42.3
4	0.58	15.7	21.0
5	0.70	68.6	191.5
6	0.79	28.0	32.2
7	0.83	111.9	127.5
8	0.97	68.7	66.5
9	1.04	91.6	105.2
10	1.23	92.5	139.5
11	1.46	100.0	100.0
12	1.72	62.2	75.5
13	2.01	28.7	23.6
14	2.32	18.4	42.6
15	2.86	32.6	38.8
16	3.38	15.4	22.2

*p,p'-DDE = 1.00

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

	Sample Size	PCB	ΣDDT*
Seawater	53	$<$10 ppt	$<$1-5 ppt
Zooplankton	7	0.01 - 0.03	0.01
Mussels	c.200	0.05 - 0.5	0.01
Norway lobster	33	0.01 - 0.1	0.01 - 0.1
Herring	154	0.01 - 2.0	0.01 - 1.0
Whiting: muscle	18	0.01 - 0.4	0.01
liver	15	1.0 - 7.0	1.0 - 2.0
Cod: muscle	5	0.3 - 1.8	0.4 - 0.52
liver	5	4.5 -50.	2.3- 12.
Other fish	83	0.1 - 1.0	0.04 -1.0
Razorbill livers	7	2. - 44.	5. - 13.
Guillemot livers:			
birds found dead	49	2.- 880.	1.7- 26.
birds shot	5	0 - 2.	0.1 - 0.8

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

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

	Baltic Sea				Stockholm Archipelago			
	Mean	Range	N	ΣDDT/PCB	Mean	Range	N	ΣDDT/PCB
Mussel	4.3	(1.9-8.6)	(40)	1.4	5.2	(3.4-7.0)	(15)	0.6
Herring	6.8	(0.5-23)	(18)	2.5	5.1	(3.3-8.5)	(4)	1.5
Seal	35.	(16-44)	(3)	3.4	30.	(16-56)	(3)	5.7
Guillemot eggs	250.	(140-360)	(9)	2.3		--		
Heron					9400.		(1)	1.5
White-tailed Eagle:								
breast muscle					14000.	(8400-17000)	(4)	1.8
brain					910.	(490-1500)	(3)	2.1
eggs					540.	(250-800)	(5)	1.9

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Scientific Names of Species Mentioned in Tables 6 & 7

Cod	Gadus morhua
Guillemot	Uria aalge
Heron	Ardea cinerea
Herring	Clupea harengus
Mussel	Mytilus edulis
Norway lobster	Nephrops
Razorbill	Alca torda
Seals	Phoca vitulina & Halichoerus grypus
White-tailed Eagle	Haliaetus albicilla
Whiting	Merluccius Merluccius

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

Area	Mean PCB Level in Fish (ppm)	ΣDDT/PCB ratio in fish and/or fish-eating Birds	Reference
U.S.: industrialized rivers	1-213	0.005-0.35	55
Lake Ontario	19	0.08-0.2	55,74
Lake Michigan	20	0.04-1	55
Lake Huron (Georgian Bay)	-	0.8	75
Lake Superior	-	2.4	75
Ontario: Lake Nipijar	0.1	4.6	75
U.S. & Canada: Prairie Lakes	<0.1	2	76
N. Quebec: Lake Minto	0.1	1	33

Table 9 PCB Levels and ΣDDT/PCB ratios in Maine Vertebrates

Area	Mean PCB Level in fish (ppm)	ΣDDT/PCB ratio in fish, fish-eating birds and/or mammals	Reference
Long Island Sound	1.2	0.08-0.18	78
Bay of Fundy	0.5	0.4	29,79,80
Atlantic Ocean	0.1	0.2 - 0.5	57
Puget Sound	0.16	1.1	56
San Francisco Bay	0.1-1.2	1-3	32,56
Californian Coast	0.02-1	5	32,56
Gulf of California	-	10	32
Gulf of Panama	-	1-2	32
Pacific Ocean (Galapagos & Hawaii)	0.03	>10	56

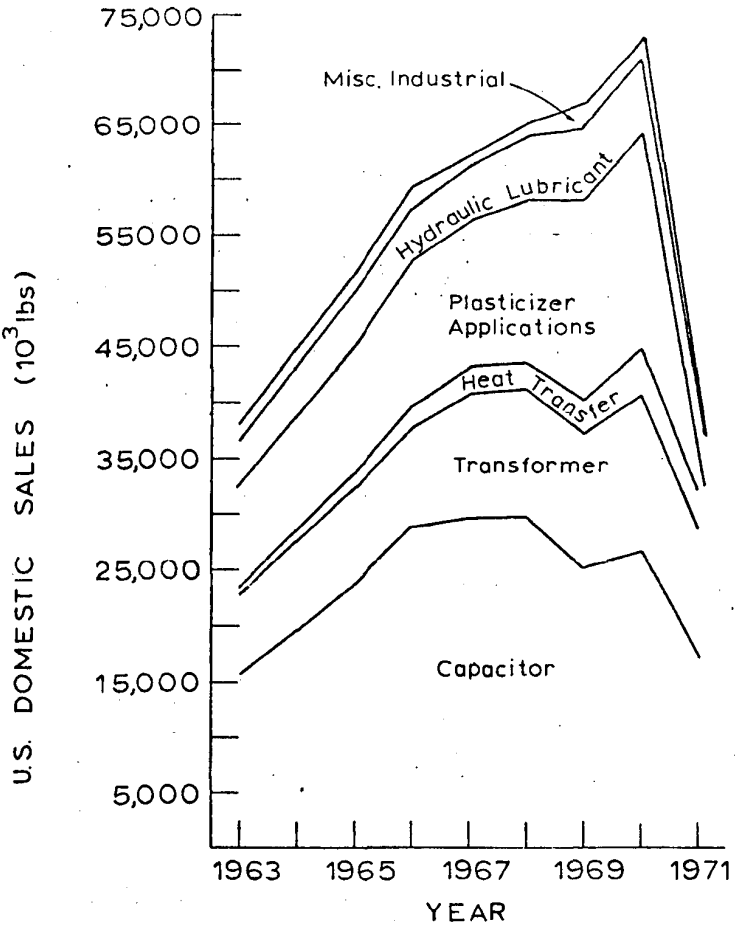

FIGURE 1 U.S. DOMESTIC SALES of PCBs by Category

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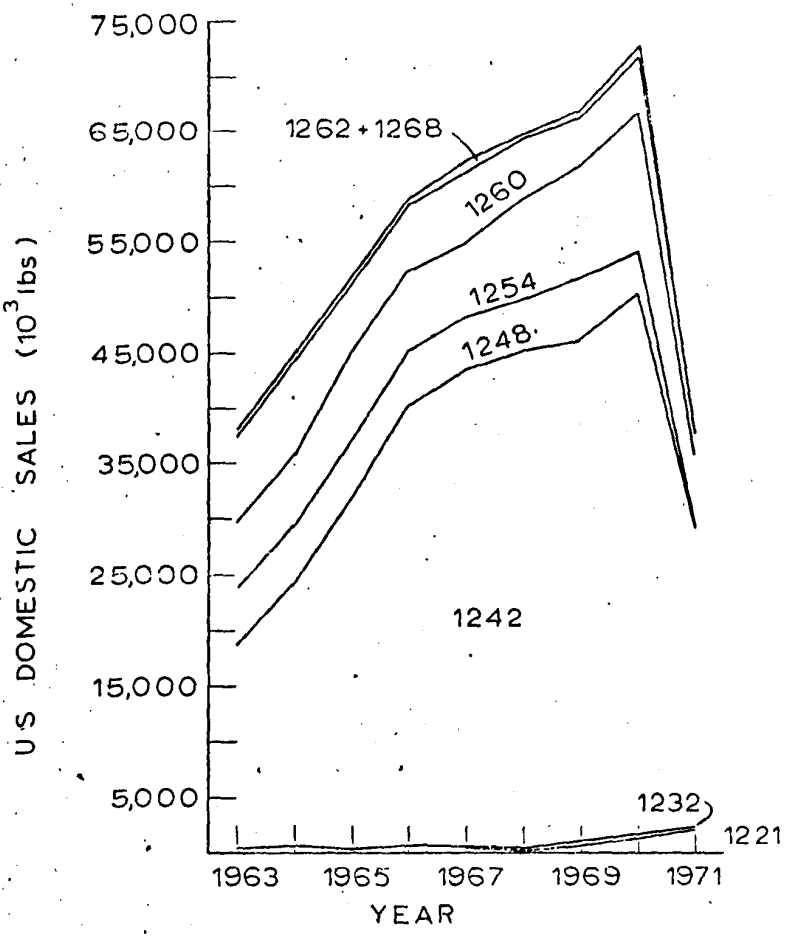

FIGURE 2 U S DOMESTIC SALES BY PCB GRADE

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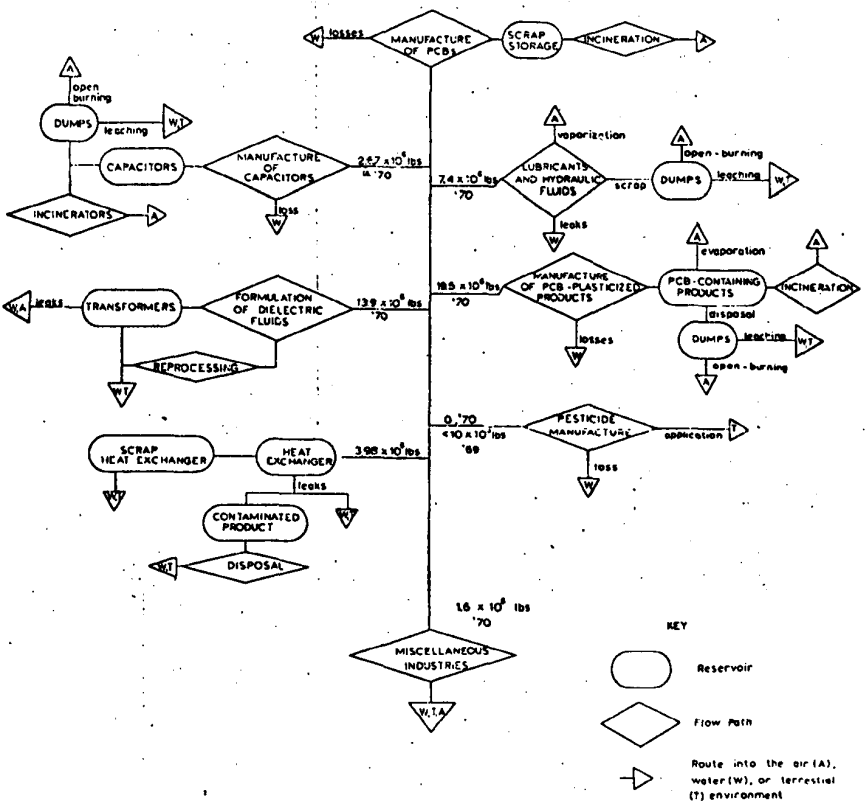

FIGURE 3

POSSIBLE ROUTES OF PCBs INTO THE ENVIRONMENT

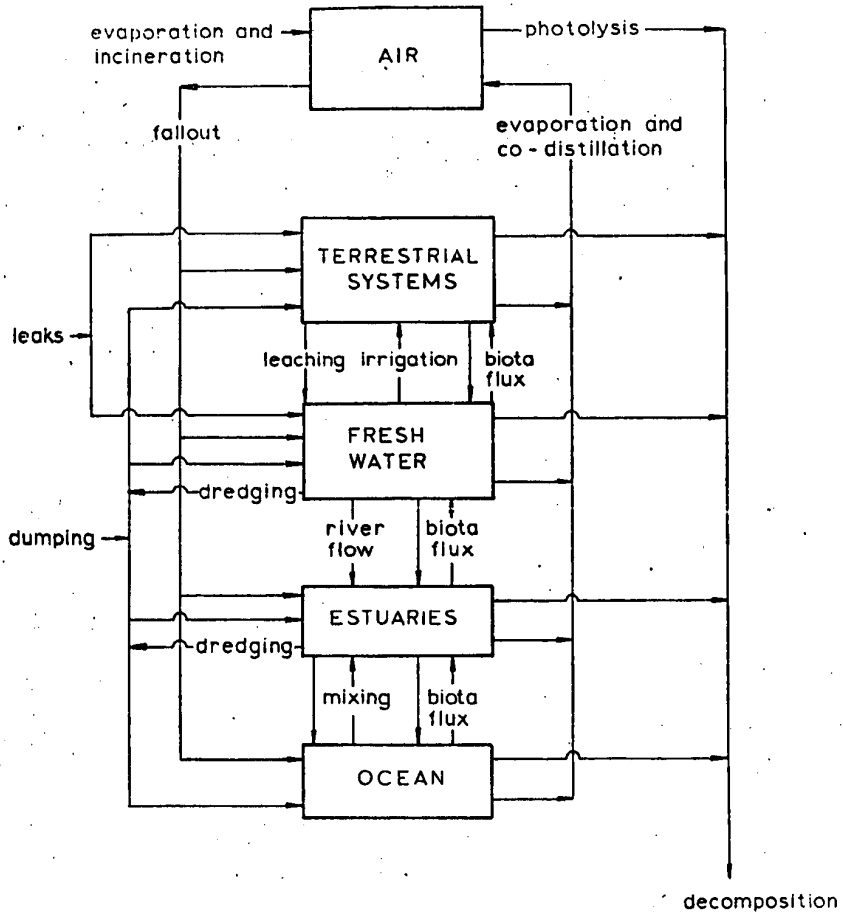

FIGURE 4 ENVIRONMENTAL TRANSPORT MODEL

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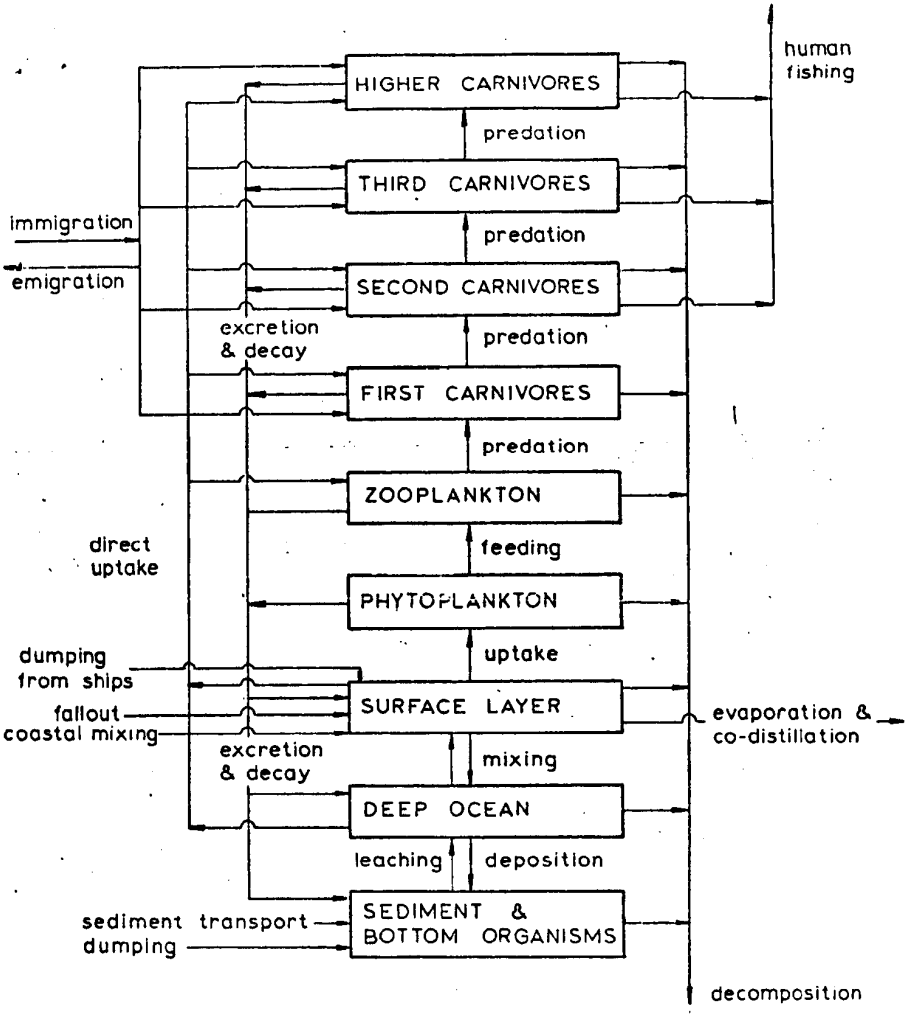

FIGURE 5 OCEAN SUB-MODEL

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