PCB's

MONS 039235

Polychlorinated biphenyls (PCB) consist of a mixture of compounds only slightly soluble in water; highly soluble in fats, oils, and nonpolar liquids; and highly resistant to both heat and biological degradation. PCB have a wide variety of industrial uses, primarily as insulating fluid in electrical and heat transfer equipment (Interdepartmental Task Force 1972).[311]

Exposure to PCB is known to cause skin lesions (Schwartz and Peck (1943)[320] and to increase liver enzyme activity that may have a secondary effect on reproductive processes (Risebrough et al. 1968,[317] Street et al. 1969,[321] Wassermann et al. 1970[325]). It is not clear at this time whether the effects are due to PCB or its contaminants, the chlorinated dibenzofurans that are highly toxic (Bauer et al. 1961,[307] Schulz 1968,[319] Verrett 1970[324]). It is also not known whether the chlorinated dibenzofurans are produced by degradation of PCB as well as during its manufacture.

The occurrence of PCB in our waters has been documented repeatedly (Von Schmidt 1965,[313] Holmes et al. 1967,[310] Risebrough et al. 1968,[317] Jensen et al. 1969,[312] Koeman et al. 1969,[312] Schmidt et al. 1971,[316] Veith and Lee 1971[323]). They have been associated with sewage effluents (Holden 1970,[309] Schmidt et al. 1971[316]) and rainwater (Tarrant and Tatton 1968),[322] as well as releases and leakage. Failures of closed systems using PCB have caused some of the more well known releases (Kuratsune et al. 1969,[314] Duke et al. 1970[308]). It has been reported that the defined treatment process does little or nothing to remove PCB (Ahling and Jensen 1970).[306]

An epidemiological study on severe poisoning by rice oil contaminated with polychlorinated biphenyls in 1968 indicated that about 0.5 grams ingested over a period of approximately one month was sufficient to cause the *Yusho* disease. Many of those affected showed no signs of relief after about three years (Kuratsune et al. 1969).[314] Price and Welch (1971)[318] have estimated on the basis of 194 samples that 41 to 45 per cent of the general population of the U.S. may have PCB levels of 1.0 mg/kg or higher (wet weight) in adipose tissue. Therefore, it appears that PCB may accumulate in the body. On this basis it can be calculated that a daily intake of 0.02 mg would require about 70 years to be toxic. Applying a factor of safety of 10 would permit a daily intake of 0.002 mg, and assuming a two liter per day intake, suggests a permissible concentration in water to be 0.001 mg/l.

However, evaluation of the retention and accumulation of PCB from water instead of oil in humans is highly desirable. A study on rats with a single oral dose of 170 mg/kg showed urinary excretion (of PCB) to be limited, while 70 per cent of the dose was found in the feces during an eight week period (Yoshimura et al. 1971).[326] Information on PCB in the diet would also be helpful.

### Conclusion

**Because too little is known about the levels in waters, the retention and accumulation in humans, and the effects of very low rates of ingestion, no defensible recommendation can be made at this time.**

MONS 039236

[illegible] Ahling, B. and S. Jensen (1970), Reversed liquid—liquid partition in determination of polychlorinated biphenyl (PCB) and chlorinated pesticides in water. *Anal. Chem.* 42(13):1483–1486.

[illegible] Bauer, H., K. H. Schulz, and U. Spiegelberg (1961), [Occupational poisonings in the production of chlorophenol compounds.] *Arch Gewerbepath.* 18:538–555.

[illegible] Duke, T. W., J. I. Lowe, and A. J. Wilson (1970) A polychlorinated biphenyl (Aroclor 1254) in the water, sediment, and biota of Escambia Bay, Florida. *Bull. Environ. Contam. Toxicol.* 5(2): 171–180.

[illegible] Holden, W. S., ed. (1970), *Water treatment and examination*, 8th ed. (Williams & Wilkins Co., Baltimore, Maryland), p. 178.

[illegible] Holmes, D. C., J. H. Simmons, J. O'G. Tatton (1967), Chlorinated hydrocarbons in British wildlife. *Nature* 216:227–229.

[illegible] Interdepartmental Task Force on PCB (1972), Polychlorinated Biphenyls in the Environment. *U.S. Department of Commerce, Washington, D. C., National Technical Information Service, Springfield, Va.* COM-72-10419.

[illegible] Jensen, S., A. G. Johnels, M. Olsson, and G. Otterlind (1969), DDT and PCB in marine animals from Swedish waters. *Nature* 224:247–250.

[illegible] Koeman, J. H., M. C. Ten Noever de Brauw, and R. H. DeVos (1969), Chlorinated biphenyls in fish, mussels and birds from [illegible]

[illegible] Kuratsune, M., Y. Morikawa, T. Hirohata, M. Nishizumi, S. Kohchi, T. Yoshimura, J. Matsuzaka, A. Yamaguchi, N. Saruta, N. Ishinishi, E. Kunitake, O. Shimono, K. Takigawa, K. Oki,



[illegible] M. Sonoda, T. Ueda, and M. Ogata (1969), An epidemiologic study on "Yusho" or chlorobiphenyls poisoning. *Fukuoka Acta Med.* 60(6):513–532.

[illegible] *New Scientist* (1966), Report of a new chemical hazard. 32:612.

[illegible] Price, H. A. and R. L. Welch (1972), Occurrence of polychlorinated biphenyls in humans. *Environmental Health Perspectives* (In press).

[illegible] Risebrough, R. W., P. Rieche, D. P. Peakall, S. G. Herman, and M. N. Kirven (1968), Polychlorinated biphenyls in the global ecosystem. *Nature* 220: 1098–1102.

[illegible] Schmidt, T. T., R. W. Risebrough, and F. Gress (1971), Input of polychlorinated biphenyls into California coastal waters from urban sewage outfalls. *Bull. Environ. Contam. Toxicol.* 6(3):235–243.

[illegible] Schulz, K. H. (1968), Clinical picture and etiology of chloracne *Arbeitsmed. Sozialmed. Arbeitshyg.* 3(2):25–29. Reprinted in translation in U.S., Congress, Senate, Committee on Commerce *Effects of 2,4,5-T on man and the environment: hearings*, 91st Cong. 2nd sess., pp. 336–341.

[illegible] Schwartz, L. and S. M. Peck (1943), Occupational acne. *New York State J. Med.* 43:1711–1718.

[illegible] Street, J. C., F. M. Urry, D. J. Wagstaff, and A. D. Blau (1968) Comparative effects of polychlorinated biphenyls and organo [illegible] 1968.

[illegible] Tarrant, K. R. and J. O'G. Tatton (1968), Organochlorine pesticides in rainwater in the British Isles. *Nature* 219:725–727.

[illegible] Veith, G. D. and G. F. Lee (1971), Chlorobiphenyls (PCBs) in the Milwaukee River. *Water Res.* 5:1107–1115.

[illegible] Varrett, J. (1970), Statement [and supporting material], in U.S. Congress, Senate, Committee on Commerce, *Effects of 2,4,5-T on the man and the environment: hearings*, 91st Cong., 2nd sess., pp. 190–360.

[illegible] Wassermann, M., D. Wassermann, I. Aronovski, I. Ivriani, and D. Rosenfeld (1970), The effect of organochlorine insecticides on serum colesterol level in people occupationally exposed. *Bull. Environ. Contam. Toxicol.* 5(4):368–372.

[illegible] Yoshimura, H., H. Yamamoto, J. Nagai, Y. Yae, H. Uzawa, Y. Ito, A. Notomi, S. Minakami, A. Ito, K. Kato, and H. Tsu (1971), Studies on the tissue distribution and the urinary and fecal excretion of $^3$H-kanechlor (chlorobiphenyls) in rats. *Fukuoka Acta Med.* 62(1):12–19.

MONS 039237

Polychlorinated Biphenyls (PCB) Polychlorinated biphenyls are chlorinated hydrocarbons which are highly resistant to chemical or biological degradation. They have been widespread environmental contaminants (Jensen et al. 1969,[180] Risebrough et al. 1968[180]). Their biological effects at present environmental concentrations are not known. PCB's can elevate microsomal enzyme activity (Risebrough et al. 1968,[180] Street et al. 1968[184]), but the environmental significance of that finding is not clear. The toxicity of PCB is influenced by the presence of small amounts of contaminated chlorinated dibenzofurans (Vos and Koeman 1970,[186] Vos et al. 1970[187]) which are highly toxic to developing embryos.

**Recommendation**

**Because of the persistence of PCB and their susceptibility to biological magnification, it is recommended that the body burdens of PCB in birds and mammals not be permitted to increase and that monitoring programs be instituted (see Section IV).**

[180] Jensen, S., A. G. Jonnels, M. Olsson and G. Otterlind (1969), DDT and PCB in marine animals from Swedish waters. *Nature* 224:247–250.

[180] Risebrough, R. W., P. Rieche, D. B. Peakall, S. G. Herman, and M. N. Kirven (1968), Polychlorinated biphenyls in the global ecosystem. *Nature* 220:1098–1102.

[184] Street, J. C., F. M. Urry, D. J. Wagstaff, and A. D. Blau (1968), Comparative effects of polychlorinated biphenyls and organochlorine pesticides in induction of hepatic microsomal enzymes. American Chemical Society, 156th National meeting, Sept. 8–12, 1968.

[186] Vos, J. G. and J. H. Koeman (1970), Comparative toxicologic study with polychlorinated biphenyls in chickens with special reference to porphyria, edema formation, liver necrosis and tissue residues. *Toxicol. Appl. Pharmacol.* 17(3):656–668.

[187] Vos, J. G., J. H. Koeman, H. L. van der Maas, M. C. ten Noever de Brauw, and R. H. de Vos (1970), Identification and toxicological evaluation of chlorinated dibenzofuran and chlorinated napthalene in two commercial polychlorinated biphenyls. *Food Cosmet. Toxicol.* 8:625–633.

MONS 039238

*TABLE III-14—Acute Toxicity of Di-n-butyl Phthalate to Four Species of Fish and Daphnia Magna.*

| Species | Temperature | LCM in µg/l 24 hr | 48 hr | 96 hr |
|---|---|---|---|---|
| Fathead minnow (Pimephales promelas) | | ..... | 1490 | 1300 (Stalling)[illegible] |
| Bluegill (Lepomis macrochirus) | | 1230 | 731 | 731 (Stalling)[illegible] |
| Channel catfish (Ictalurus punctatus) | | 3720 | 2910 | 2910 (Stalling)[illegible] |
| Rainbow trout (Salmo gairdneri) | | ..... | ..... | 6870 (Sanders)[illegible] |
| Daphnia magna | | ..... | ..... | >1000 (Sanders)[illegible] |

## POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (PCB) have been found in fish and wildlife in many parts of the world and at levels that may adversely affect aquatic organisms (Jensen et al. 1969;[374] Holmes et al. 1967;[375] Koeman et al. 1969;[376] Risebrough et al. 1968).[380] The environmental occurrence, uses, and present toxicological aspects of PCB were recently reviewed by Peakall and Lincer (1970),[384] Gustafson (1970),[372] Risebrough (1970),[387] and Reynolds (1971).[385]

Biphenyls may have 1 to 10 attached chlorine atoms, making possible over 200 compounds (Gustafson 1970).[372] PCB occur as residues in fish, and presumably also in water, as mixtures of chlorinated biphenyl isomers as shown in Table III-15 (Stalling and Johnson, *unpublished data* 1970,[376] Stalling *in press*[392]).

Analysis of PCB has been accomplished by gas chromatography after separation of PCB from pesticides. A separation method has been described by Armour and Burke (1970)[381] and modified by Stalling and Huckins (1971).[391] A method using separation on a charcoal column has shown good reproducibility (Frank and Rees, *personal communication*).[385] No standardized gas-liquid chromatography method has been proposed for the analysis of mixtures of PCB in environmental samples. The solubility of these formulations in water has not been precisely determined, but it is in the range of 100 to 1,000 µg/l (Papageorge 1970).[383] Since PCB have gas chromatographic characteristics similar to many organochlorine pesticides, they can cause serious interference in the gas chromatographic determination of chlorinated insecticides (Risebrough et al. 1968).[380]

The Monsanto Company, the sole manufacturer of PCB

MONS 039239

*TABLE III-15—Composition of PCB Residues in Selected Fish Samples from the 1970 National Pesticide Residue Monitoring Program*

| River | Location | Species | PCB Residue as Aroclor® type (µg/g whole body) 1222 | 1248 | 1254 | 1260 | Total |
|---|---|---|---|---|---|---|---|
| Ohio | Cincinnati, O. | Carp Cyprinus carpio | 10 | 70 | 42 | 8.0 | 123 |
| Ohio | Cincinnati, O. | White crappie Pomoxis annularis | 10 | 17 | 27 | 8.0 | 62 |
| Ohio | Marietta, O. | Channel catfish Ictalurus punctatus | 30 | 42 | 11 | 4.0 | 77 |
| Ohio | Marietta, O. | Channel catfish | 10 | 5.2 | 13 | 4.0 | 32 |
| Yazoo | Redwood, Miss. | Smallmouth buffalo Ictiobus bubalus | 73 | ..... | 1.4 | ..... | 73 |
| Hudson | Poughkeepsie, N.Y. | Goldfish Carassius auratus | 8 | 179 | 32 | ..... | 213 |
| Neuse | Nelson, Pa. | Walleye Stizostedion vitreum v. | ..... | 9.2 | 25 | 4.6 | 33 |
| Delaware | Camden, N.J. | White perch Roccus americanus | ..... | 8.8 | 9.0 | 1.9 | 19 |
| Cape Fear | Elizabeth Town, N.C. | Gizzard shad Porosoma cepedianum | 19 | ..... | 2.6 | 1.1 | 23 |
| Lake Ontario | Port Dalhousie, N.Y. | White perch | 13 | ..... | 4.6 | [illegible] | 19 |
| Mississippi | Memphis, Tenn. | Drum Aplodinotus grunniens | 11 | ..... | 4.5 | 1.4 | 19 |
| Merrimac | Lowell, Mass. | Drum | [illegible] | 75 | 9.1 | 3.2 | 90 |

[illegible] are manufactured under the trademark Aroclor® 1200 and 5400, and a mixture of bi- and terphenyls [illegible] Aroclor® 4465. The known composition and chromatographic characteristics of each formulation have been described by Stalling and Huckins (1971)[221] and Bagley et al. (1970).[170] A contaminant of some PCB, especially those manufactured in Europe, are chlorinated dibenzofurans (Brunger *personal communication* 1972).[201] Although these byproducts would appear to be extremely toxic, no data are available on their toxicity to aquatic life.

### Direct Lethal Toxicity

Studies of toxicity of PCB to aquatic organisms are limited. They show considerable variation of toxicity to different species, as well as variation with the chlorine content of the PCB. Nevertheless, some trends in the toxic characteristics have become apparent, principally from the work of Mayer as described below:

- The higher the per cent chlorine, the lower the apparent toxicity of PCB to fish (Mayer, *in press*).[179] This was found in 15-day intermittent-flow bioassays using bluegills (*Lepomis macrochirus*) and channel catfish (*Ictalurus punctatus*) with Aroclor® 1242, 1248, 1254. All LC50 values were in the range 10 to 300 µg/l.
- The bluegill/channel catfish experiments also illustrated that all LC50 values decreased significantly when exposures continued from 15 to 20 days. The 96-hour LC50 of a PCB to fish cannot adequately measure its lethal toxicity.
- The same tests showed that the toxicity of Aroclor® 1248 doubled when the temperature was raised from 20 C to 27 C.

To invertebrates, Aroclor® 1242 has about the same acute toxicity that it has to fish. In 4- and 7-day tests (Saunders, *in press*),[180] it killed *Gammarus* at 42 µg/l and crayfish (*Cambarus*) at 30 µg/l, with values that were similar to the 15-day LC50 reported for bluegills. However, there [illegible] an extreme range in the reported short-term lethal levels [illegible] Aroclor® 1254 for invertebrates. Saunders (*in press*)[180] reported a 96-hour LC50 as 80 µg/l for crayfish and only [illegible] µg/l for glass shrimp (*Paleomonetes*) in 7-day tests; and [illegible] al. (1970)[171] reported that as little as 0.94 µg/l [illegible] mature pink shrimp (*Panaeus duorarum*). Part of this [illegible] related to exposure periods in the tests; part [illegible] [illegible] [illegible]

[illegible] two species of [illegible] and [illegible] *xanthurus*, [illegible] that [illegible] [illegible] [illegible] [illegible] exposure rate in water [illegible] [illegible] [illegible] [illegible]

[illegible] and [illegible] earth [illegible] *Nature* 227:91–112.

[illegible] Armour, J. A. and J. A. Burke (1970), Method for separating polychlorinated biphenyls from DDT and its analogs. *J. Assoc. Offic. Anal. Chem.* 53(4):761–768.

[illegible] Bagley, G. E., W. L. Reichel, and E. Cromartie (1969), Identification of polychlorinated biphenyls in two bald eagles by combined gas-liquid chromatography-mass spectrometry. *J. Ass. Offic. Anal. Chem.* 53(2):251–261.

[illegible] Duke, T. W., J. I. Lowe, and A. J. Wilson, Jr. (1970), A polychlorinated biphenyl (Aroclor 1254®) in the water, sediment, and biota of Escambia Bay, Florida. *Bull. Environ. Contam. Toxicol.* 5(2):171–180.

[illegible] Gustafson, C. G. (1970), PCB's–prevalent and persistent. *Environ. Sci. Technol.* 4:814–819.

[illegible] Hansen, D. J., P. R. Parrish, J. I. Lowe, A. J. Wilson, Jr., and P. D. Wilson (1971), Chronic toxicity, uptake, and retention of a polychlorinated biphenyl (Aroclor 1254) in two estuarine fishes. *Bull. Environ. Contam. Toxicol.* 6(2):113–119.

[illegible] Holden, A. V. (1970), International cooperative study of organochlorine pesticide residues in terrestrial and aquatic wildlife 1967/1968. *Pestic. Monit. J.* 4(3):117–135.

[illegible] Holmes, D. C., J. H. Simmons, and J. O'G. Tatton (1967), Chlorinated hydrocarbons in British wildlife. *Nature* 216:227–229.

[illegible] Jensen, S. A., G. Johnels, S. Olsson, and G. Otterlind (1969), DDT and PCB in marine animals from Swedish waters. *Nature* 224:247–250.

[illegible] Jensen, S., N. Johansson, and M. Olsson (1970), PCB-indications of effects on salmon, [illegible] Conference, Stockholm, September 28, 1970. (Swedish Salmon Research Institute), (Report [illegible] 7/1970).

[illegible] Koeman, J. H., M. C. Ten Noever de Brauw, and R. H. De Vos (1969), Chlorinated biphenyls in fish, mussels and birds from the River Rhine and the Netherlands coastal area. *Nature* 221: 1126–1128.

[illegible] Mayer, F. L., Jr. *in press* (1972), Special report on PCB's in Progress in sport fishery research, 1970. (Government Printing Office, Washington, D. C.)

[illegible] Mulhern, B. M., E. Cromartie, W. L. Reichel, and A. A. Belisle (1971), Semi quantitative determination of polychlorinated biphenyls in tissue samples by thin layer chromatography. *J. Ass. Offic. Anal. Chem.* 54(3):548–550.

[illegible] Nebeker, A. V., F. A. Puglis and D. L. Defoe (1971), Toxicity of polychlorinated biphenyls (PCB) to fish and other aquatic life. Final draft. *Environmental Protection Agency, National Water Quality Laboratory*, Duluth, Minnesota.

[illegible] Nimmo, D. R., P. D. Wilson, J. R. Blackman, and A. J. Wilson, Jr. (1971), Polychlorinated biphenyl absorbed from sediments by fiddler crabs and pink shrimp. *Nature* 231:50–52.

[illegible] Papageorge, W. B. (1970), Monsanto Company, presented in part at a meeting, "PCB's in the environment," March 17, 1970, sponsored by the National Water Quality Laboratory, FWQA, Duluth, Minnesota.

[illegible] Peakall, D. B. and J. L. Lincer (1970), Polychlorinated biphenyls–another long-life widespread chemical in the environment. *Bioscience* 20:958–964.

[illegible] Reynolds, L. M. (1971), Pesticide residue analysis in the presence of polychlorobiphenyls (PCB's). *Residue Rev.* 34:27–57.

[illegible] Risebrough, R. W., P. Pieche, D. B. Peakall, S. G. Herman, and M. N. Kirven (1968), Polychlorinated biphenyls in the global ecosystem. *Nature* 220.1097–1102.

[illegible] Risebrough, R. (1970), Man-made waters in the wind. *Environment* 12(1): 16–26.

[illegible] PCB's, in Proceedings [illegible] Printing Office, [illegible]).

[illegible] Special Report on PCB's. In *Proceedings* [illegible] of Sport Fisheries and Wildlife, Washington, D.C. [illegible]).

[illegible] Stalling, D. L. and F. L. Mayer, Jr. (1970), Toxicities of PCB's to fish and environmental residues. *Environmental Health Laboratory* 154–165.

[illegible] Stalling, D. L. and J. L. Johnson (1971), Gas-liquid chromatography-mass spectrometry characterization of polychlorinated biphenyls (aroclors) and $^{36}$Cl-labeling of Aroclors 1248 and 1254. *J. Ass. Offic. Anal. Chem.* 54(4):801–807.

[illegible] Stalling, D. L. *in press* (1971), Analysis of Organochlorine Residues in Fish. Current Research at the Fish-Pesticide Research Laboratory, Conference on Pesticide Chemistry. Tel Aviv, Israel.


## References Cited


[illegible] Brungs, W. A., *personal communication*, 1972. Effects of polychlorinated biphenyls on aquatic life.

[illegible] Mehrle, P. M. and B. F. Grant, *unpublished data*, 1971. Fish Pesticide Research Laboratory, Columbia, Missouri.

[illegible] Frank, R. and J. Rees, *personal communication*. R. Frank, Director of Provincial Pesticide Residue Testing Laboratory, University of Guelph, Guelph, Ontario, Canada; J. Rees, Ontario Water Resources Commission, Toronto, Ontario, Canada.

[illegible] Stalling, D. L. and J. L. Johnson, *unpublished data*, 1970. Laboratory Crosscheck analyses from the 1970 National Pesticide Monitoring Program. Fish Pesticide Research Laboratory, Columbia, Missouri.

[illegible] Stalling, D. L. and J. A. Hudson, *unpublished data*, 1971. National Pesticide Monitoring Program. Fish Pesticide Research Laboratory, Columbia, Missouri.


MONS 039242

## TOXIC ORGANICS

The toxic organics constitute a considerable variety of chemical compounds, almost all of which are synthetic. The total production of synthetic organic chemicals in the U.S. in 1968 was 120,000 million pounds, a 15 per cent increase over 1967; 135,000 million pounds were produced in 1969, a 12 per cent increase over 1968 (United States Tariff Commission 1970).[377] This figure, in the order of $5 \times 10^{18}$ grams, may be compared with the total productivity of the sea, which is in the order of $2 \times 10^{16}$ grams of carbon incorporated into phytoplankton per year (Ryther 1969).[373] When considered in a global and future context, the production of synthetic chemicals by man cannot be considered an insignificant fraction of nature's productivity.

The majority of the synthetic organic chemicals, including those considered toxic, are readily degradable to elementary materials which reenter the chemical cycles in the biosphere. These pose no long-term hazard if applied or released into the environment in quantities sufficiently small to meet the recommendations for mixing zones (see p. 51).

The [illegible] pounds that enter the environment, whether they are introduced incidentally as waste materials or deliberately through their use. The toxicity, chemical stability, and resistance to biological degradation of such chemicals are factors that must be considered in assessing their potential effects on ecosystems. Moreover, because of the partitioning of nonpolar compounds among the components of marine ecosystems, relatively high concentrations of these, including halogenated hydrocarbons, are frequently found in organisms.

Only recently it was discovered that polychlorinated biphenyls (PCB), a class of chlorinated hydrocarbons used in a variety of industrial applications, were widespread contaminants in marine ecosystems (Duke et al.).[334a] Concentrations up to or higher than 1000 ppm in the body fat of estuarine birds have been recorded in both Europe and North America (Risebrough et al. 1968,[371] Jensen et al. 1969[380]). Moreover, both DDT and PCB have been found in organisms from depths of 3200 meters in the open North Atlantic Ocean (Harvey et al. 1972).[339]

The discovery of a man-made contaminant such as PCB, unknown in the environment a few years ago, in such unexpectedly high concentrations in marine organisms raises several questions. Are the concentrations of these compounds still increasing in the marine environment and at what rate, and what are the long-term effects upon the marine communities? Is it possible that other pollutants, undetected by the methodology that measures the chlorinated hydrocarbons, are present in comparable amounts?

Criteria employed in the past to protect freshwater ecosystems were based on data now seen to be inadequate and on an approach that looked at pollutant concentrations in waste water effluents rather than in the receiving system. Evidently it is necessary to attempt to relate the amounts of input into the ecosystem to the levels in the various components of the ecosystem, including indicator organisms. The concentrations of a persistent pollutant in an indicator organism are considered the best way of following accumulation trends in an aqueous ecosystem that serves as a sink for the pollutant, once the capacity of the ecosystem to absorb the pollutant has been determined. If the concentrations in the indicator organisms exceed those considered safe for the ecosystem, input should then be reduced, restricted, or eliminated until environmental levels are acceptable on the basis of established criteria. Inputs of persistent pollutants into the marine environment, however, are in many cases indirect and not immediately controllable, e.g. river runoffs, atmospheric fallout, and dumping by foreign and domestic ships. The sources of the chemicals in atmospheric fallout may be located anywhere in the world.

Different recommendations must therefore be developed to protect the marine environment from increasing amounts and varieties of organic pollutants that might be anticipated over the next century. The same recommendations may be applied to estuaries, but these must also be protected from a variety of chemicals that are less persistent and pose no long-term hazard, but that may, because of toxic effects upon organisms, cause unacceptable amounts of damage. These include many of the pesticides, components of sewage, biological wastes from slaughter houses, and other organic wastes from industry.

Acute toxicity values and subacute effects of pesticides on marine life are listed in Appendix III–Table 6, and in Table IV–7, p. 163. Table IV–6 is a summary of the "most sensitive" organisms taken from Appendix III–Table 6 and includes a list of chemicals that are considered to have potential environmental importance in estuarine or marine ecosystems. The list includes many of the pesticides that are readily degradable in the environment but because of their high toxicity are potentially dangerous to estuarine ecosystems. The list, which should be revised as new data become available, proposes a minimum number of such chemicals. Appendix III–Table 6 includes the following information relative to the potential importance of each material as coastal and marine contaminants. (a) Production figures, which are taken from the 1969 Tariff Commission reports, are listed in the second column. The production figures provide a useful clue to the compounds that are of potential importance as marine pollutants. The order of the chemicals generally follows that of the Tariff Commission reports and is not intended to be a ranking in order of importance. (b) The third column of the table indicates



MONS 039243

[illegible] not the compound has been detected in the water or in marine organisms. Compounds which have been detected are of greater immediate concern than those which have not. [redacted] their low solubility in water. [redacted] compounds which are biologically [redacted] in an organism but not in the water [redacted] (c) The fourth column, trophic accumulation, indicates whether the compound has been shown to pass through the food web from prey species to predator. Compounds that are so accumulated are of greater concern than compounds of comparable toxicity which are not. Finally, the species thought to be most sensitive to the compound are indicated in the final columns with reference to original studies in the scientific literature. These data are useful as a guide only and are not sufficient in themselves for definitive evaluation of the environmental significance of each compound.

The report, "The Effects of Chemicals on Aquatic Life, vol. 3, Environmental Protection Agency, Water Quality Office, 1971," has been useful as a guide to the available toxicity data of industrial chemicals on marine organisms. Appendix III–Table 6 is a compendium of data on toxicity of pesticides to marine organisms. These sources are incomplete and should be continually revised.

**Bases for Recommendations**

1. In order to provide an adequate level of protection for commercially important marine species and for species [redacted] Section III, p. 40.) It assumes that a concentration of one one-hundredth (0.01) of that causing harm to the most sensitive species to be protected will not damage this species or the ecosystem. Future studies may show that the application factor must be decreased or increased in magnitude.

2. The application factor may also be used for the compounds that are trophically accumulated in food webs in order to protect fish and invertebrates to which these compounds are toxic. It cannot be used, however, to protect fish-eating birds and mammals which may trophically accumulate these compounds from their prey species, in part because sublethal effects [redacted] hormone imbalance may adversely affect reproductive capacity and therefore the long term survival of populations. Levels that would protect fish-eating birds and mammals against the effects of compounds that are trophically accumulated from prey species are given in the discussion of Marine Wildlife (see pp. 31–43).

The recommendations below apply to all organics of both proved and potential toxicity.

**Recommendations**

In general, marine life with the exception of fish-eating birds and mammals should be protected where the maximum concentration of the chemical in the water does not exceed one one-hundredth (0.01) of the LC50 values listed in Column 7, Table IV–7, p. 158. If new data indicate that an ecosystem can adequately degrade a particular pollutant, a higher application factor for this pollutant may be used.

In order to maintain the integrity of the ecosystem to the fullest possible extent, it is essential to consider effects on all non-target organisms when applying pesticides to estuarine habitats in order to control one or more of the noxious species. For those occasions when chemicals must be used, the following guidelines are offered:

- a compound which is the most specific for the intended purpose should be preferred over a compound that has broad spectrum effects;
- a compound of low persistence should be used in preference to a compound of greater persistence;
- a compound of lower toxicity to non-target organisms should be used in preference to one of higher toxicity;
- water samples to be analyzed should include all suspended particulate and solid material: residues associated with these should therefore be considered as present in the water;
- when a derivative such as p,p′-DDE or 1-napthol is measured with or instead of the parent compound, the toxicity of the derivative should be considered separately: if the toxicity of a derivative such as an ionic species of a pesticide is considered equivalent to that of the original parent compound, concentrations should be expressed as equivalents of the parent compound.

It is recommended that the chemicals listed in Table IV–7 and all chemicals subsequently added to this list be considered as toxic organic compounds potentially harmful to the marine environment. It is emphasized that the data in Table IV–7 are not sufficient in themselves for final evaluation of the environmental significance of each compound.

disproven

MONS 039244

TABLE [illegible] [illegible] [illegible]

... D. ..., R. ... Wellman and ... inter... Seven ... Crab ... J. ...

... J. E. Johnson and F. A. ... (1963) ... in ... levels in the eastern ... from ... Act ... Pesticide Monitoring J. ...

... Cade, T. J., J. L. Lincer, C. M. White, D. G. ... and ... Swartz (1970), DDE ... and eyelid ... in ... falcons and hawks. *Science* 172: 955–957.

... Caspe, V. L. (1967), Galveston Bay pesticide study—... oyster samples analyzed for pesticide ... following ... control program. *Pesticides Monitoring J.* 1(2): 15.

... Chin, E. and D. M. Allen (1958), Toxicity of ... insecticides to two species of shrimp, *Penaeus setiferus* and *Leucosolenia setiferus*. *Tex. J. Sci.* 9(3):270–278.

... Davis, H. C. and H. Hidu (1969) Effects of ... pesticides on embryonic development of clams and oysters and on survival and growth of the larvae. *Fish. Bull.* 67(2):393–404.

... Duke, T. W., J. I. Lowe and A. J. Wilson, Jr. (1970), A polychlorinated biphenyl (Aroclor® 1254) in the water, sediment, and biota of Escambia Bay, Florida, *Ecol. Bull., Environ. Contam. Toxicol.* 5(2):171–180.

... Eisler, R. (1969), Acute toxicities of insecticides to marine decapod crustaceans. Crustaceana 16(3):302–310.

... Eisler, R. (1970a), Factors affecting pesticide-induced toxicity in an estuarine fish. *Technical Papers of Bur. Sport. Fish. Wild.* 45:20 p.

... Eisler, R. (1970b), Acute toxicities of organochlorine and organophosphorus insecticides to estuarine fishes. Technical Papers of Bur. Sport Fish. Wildl. 46:12 p.

... Erickson, S. J., T. E. Maloney and J. H. Gentile (1970) Effect of ... phytoplankton. J. Water Pollution Control Federation 42(8): R-329-335, Part 2.

... Harvey, G. R., V. T. Bowen, R. H. Backus and G. D. Grice (1972), Chlorinated hydrocarbons in open-ocean Atlantic organisms. *Proceedings of the Colloquium "The Changing Chemistry of the Oceans"* (In press).

... Jensen, S., A. G. Johnels, M. Olsson, and G. Otterlind (1969), DDT and PCB in marine animals from Swedish waters. *Nature* 224:247–250.

... Jensen, S., A. Jernelov, R. Lange, and K. H. Palmork (1970), Chlorinated byproducts from vinyl chloride production: A new source of marine pollution. F. A. O. Technical Conference Marine Pollution and its Effects on Living Resources and Fishing. Rome, Italy, December, 1970.

... Katz, M. (1961), Acute toxicity of some organic insecticides to three species of salmonids and to the threespine stickleback. *Trans. Amer. Fish. Soc.* 90(3):264–268.

... Koeman, J. H., and H. Genderen (1970), Tissue levels in animals and effects caused by chlorinated hydrocarbon insecticides, biphenyls and mercury in the marine environment along the Netherlands coast. F. A. O. Technical conference on Marine Pollution and its Effects on Living Resources and Fishing. Rome, *Italy, December, 1970.*

... Korschen, L. J. (1970) Soil-food-chain-pesticide wildlife relationships in aldrin treated fields. *J. Wildl. Manag.* 34:186–199.

... Krantz, W. C., B. M. Mulhern, G. E. Bagley, A. Sprunt, IV, F. J. Ligas, and W. B. Robertson, Jr., (1970), Organochlorine and heavy metal residue in Bald Eagle Eggs. *Pesticides Monitoring J.* 4:136–140.

... Lowe, J. I., P. R. Parrish, A. J. Wilson, Jr., J. ... on, and T. W. Duke. (1971) Effects of mirex on selected ... marine or-

... *... Research ...* ... Fish., ... and Oce..., ... 171–183.

... G. (1964) ... ted hydrocarbons noticed ... ... and ... *Pesticides Monitoring J.* 1:1–7.

... Marine Water Quality Lab. (CSIRO) ... ... dissolution of ... toxicity of natural ... Progress ... F. W. Q. A. T. ... Bull. ...

... Nisbet, D. R., A. J. Wilson, Jr. and ... Blackmon ... Localization of DDT in the body organs of ... and white ... *Bulletin of Environmental Contamination and Toxicology* 5(4): ...

... Nimmo, D. R., P. D. ... R. R. Blackman and A. J. ... Jr. (1971) Polychlorinated biphenyl ... from ... by ... crabs and pink shrimp. *Nature* 231:50–52.

... Risebrough, R. W., P. Rieche, D. B. Peakall, S. G. Herman, and M. N. Kirven (1968), Polychlorinated biphenyls in the global ecosystem. *Nature* 220:1098–1102.

... Rowe, D. R., L. W. Canter, P. J. Snyder and J. W. Mason (1971), Dieldrin and endrin concentrations in a Louisiana estuary. *Pesticides Monitoring J.* 4:177–183.

... Ryther, J. H. (1969), Photosynthesis and fish production in the sea. *Science* 166:72–76.

... Schreiber, R. W. and R. W. Risebrough (1972, *in press*), Studies of the Brown Pelican *Pelecanus occidentalis*. *Wilson Bulletin.*

... Tatton, J. O'G. and J. H. A. Ruzicka (1967). Organochlorine pesticides in Antarctica. *Nature* 215 (5099):346–348.

... Ukeles, Raveana (1962) Growth of pure cultures of marine phytoplankton in the presence of toxicants. *Appl. Microbiol.* 10(6): 532–537.

... U.S. Tariff Commission (1970), *Synthetic organic chemicals, United States production and sales, 1968* [TC publication 327] (Government Printing Office, Washington, D. C.), 266 p.

... Vos, J. G., H. A. Breeman and H. Benschop (1968), The occurence of the fungicide hexachlorobenzene in wild birds and its toxico- ...

... Walsh, G. E. (1972), Effects of herbicides on photosynthesis and growth of marine unicellular algae. *Hyacinth Control J.* 10:45–48.

... Wolman, A. A. and A. J. Wilson (1970), Occurence of pesticides in whales. *Pesticides Monitoring J.* 4:8–10.

MONS 039246

Polychlorinated Biphenyls (PCB)

Evidence is accumulating that PCB [illegible] to the shell thinning that has been a major [illegible] reproductive failures and population [illegible] and fish-eating birds. Dietary PCB produced [illegible] ning of eggs of Mallard Ducks (*Anas platyrhynchos*) (Heath et al. *in press* 1972),[45] nor did PCB have any effects on eggs of Ring Doves (*Streptopelia risoria*) (Peakall 1971).[46] A PCB effect could not be associated with the thinning of Brown Pelican (*Pelecanus occidentalis*) eggshells (Risebrough *in press* 1972).[47] PCB may increase susceptibility to infectious agents such as virus diseases (Friend and Trainer 1970).[48] Like other chlorinated hydrocarbons, PCB increases the activity of liver enzymes that degrade steroids, including the sex hormones (Risebrough et al. 1968;[49] Street et al. 1968).[47] The ecological significance of this phenomenon is not clear.

Because laboratory studies have indicated that PCB, with its derivatives or metabolites, causes embryonic death of birds (Vos et al. 1970;[74] Vos and Koeman 1970;[74] Vos *in press* 1972;[72] Peakal et al. *in press* 1972[50]) and because exceptionally high concentrations are occasionally found in fish-eating and raptorial species (Risebrough et al. 1968;[44] Jensen et al. 1969[45]), it is highly probable that PCB has had an adverse effect on the reproductive capacity of some species of birds that have shown population declines.

Median PCB concentrations in whole fish of eight species from Long Island Sound, obtained in 1970, were in the order of one milligram per kilogram (mg/kg) (Hays and Risebrough 1972),[47] and comparable concentrations have been reported from southern California (Risebrough 1969).[51] On the basis of the high probability that PCB in the environment has contributed to the reproductive failures of fish-eating birds, it is desirable to decrease these levels by at least a factor of two (see Section III on Freshwater Aquatic Life and Wildlife pp. 203–213).

**Recommendation**

**It is recommended that PCB concentrations in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or [redacted]**

**In the absence of a standardized methodology for the determination of PCB in environmental samples, it is recommended that estimates of PCB concentrations be based on the commercial Aroclor® preparation which is most closely resembles in chlorine composition. If the PCB composition should resemble a mixture of more than one Aroclor®, it should be considered a mixture for the basis of quantitation, and the PCB concentration reported should be the sum of the component Aroclor® equivalents.**

[illegible]

[illegible]

[illegible]

Appendix II-2

## Pesticides Recommended for Monitoring in the Environment

| Common or trade name | Chemical name |
|---|---|
| **Pesticides Recommended for Monitoring** | |
| Aldrin | 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene |
| Azinphos-methyl (Guthion®) | O,O-dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl) phosphorodithioate |
| Benzene hexachloride (BHC) | 1,2,3,4,5,6-hexachlorocyclohexane; gamma isomer is commercial insecticide called lindane, also called gamma-hexachlorocyclohexane |
| Captan | N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide |
| Chlordane | at least 60 percent of 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene and not over 40 percent of related compounds |
| 2,4-D (2,4-dichlorophenoxyacetic acid) | (2,4-dichlorophenoxy)acetic acid |
| DDT (technical DDT is a mixture of similar compounds produced by the condensation of chlorobenzene with chloral) | 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane; technical DDT consists of a mixture of 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane and the o,p'-isomer (in a ratio of 1:3 to 1:4 or 1 to 1) |
| Dicamba | 3,6-dichloro-o-anisic acid |
| Dieldrin | not less than 85 percent of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene |
| **Dithiocarbamate pesticides:** | |
| Maneb | [(ethylenebis(dithiocarbamato))manganese] |
| Nabam | sodium ethylenebis(dithiocarbamate) |
| Zineb | [(ethylenebis(dithiocarbamato))zinc] |
| Endrin | 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-exo,endo-5,8-dimethanonaphthalene |
| Heptachlor | 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene |
| Heptachlor epoxide | 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene |
| Lindane | 1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer of not less than 99 percent purity |
| Malathion | diethyl mercaptosuccinate S-ester with O,O-dimethyl phosphorodithioate |
| **Organo-metallic pesticides (inorganic and organic):** | |
| Methoxychlor | 1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane; technical methoxychlor contains not less than 80 percent of this isomer also |
| Methyl parathion | O,O-dimethyl O-(p-nitrophenyl) phosphorothioate |
| Mirex | dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene |
| Monitor (Plantvax®) | 4-(methylamino)-O-(2,6-dichloro-m-tolyl)propionothioate |
| Parathion | O,O-diethyl O-(p-nitrophenyl) phosphorothioate |
| PCNB | pentachloronitrobenzene |
| Perthane | 4,4'-(2,2-dichloroethylidene)bis(ethylbenzene) |
| Silvex | 2-(2,4,5-trichlorophenoxy)propionic acid |
| Strobane® | terpene polychlorinates; technical strobane is a complex mixture of polychlorinated camphenes and related compounds with an average chlorine content of approximately 67 percent |
| 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) | (2,4,5-trichlorophenoxy)acetic acid |
| TDE (DDD) (technical TDE is a mixture of similar compounds produced by the condensation of chlorobenzene with dichloroethanol) | 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane; technical TDE contains at least 90 percent of this isomer and the o,p'-isomer (in a ratio of 3:1 to 4:1) |
| Toxaphene | chlorinated camphene containing 67-69 percent chlorine |
| 2,4,5-TP (Silvex) | 2-(2,4,5-trichlorophenoxy)propionic acid |

| Common or trade name | Chemical name |
|---|---|
| **Substituted Urea Pesticides for Monitoring** | |
| DCMU (Direx®) | 3-(3,4-dichlorophenyl)-1,1-dimethylurea |
| Diuron | 3-(3,4-dichlorophenyl)-1,1-dimethylurea |
| Dymuron (Dymid®) | 1-methyl-3-phenyl-1-(p-tolyl)urea |
| Fenuron | 1,1-dimethyl-3-phenylurea |
| Monuron (Telvar®) | 3-(p-chlorophenyl)-1,1-dimethylurea |
| Neburon | 1-butyl-3-(3,4-dichlorophenyl)-1-methylurea |
| Siduron | 1-(2-methylcyclohexyl)-3-phenylurea |
| Tebuthiuron | N-[5-(1,1-dimethylpropyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea |
| **Halogenated Aliphatic Acid Herbicides:** | |
| Dalapon | 2,2-dichloropropionic acid |
| Fenac | 2,3,6-trichlorophenylacetic acid |
| TCA | trichloroacetic acid |
| **Miscellaneous Herbicides:** | |
| Amitrole | 3-amino-s-triazole |
| Bromacil | 5-bromo-3-sec-butyl-6-methyluracil |
| Diquat | 6,7-dihydrodipyrido(1,2-a:2',1'-c)pyrazinediium ion |
| Endothall | 7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid |
| Paraquat | 1,1'-dimethyl-4,4'-bipyridinium ion |
| Picloram | 4-amino-3,5,6-trichloropicolinic acid |
| Simazine | 2-chloro-4,6-bis(ethylamino)-s-triazine |
| Terbacil | 5-chloro-3-tert-butyl-6-methyluracil |
| **Miscellaneous Pesticides:** | |
| Chlorobenzilate | ethyl 4,4'-dichlorobenzilate |
| Dicofol (Kelthane®) | 4,4'-dichloro-α-(trichloromethyl)benzhydrol |
| Dinocap | 2,6-dinitro-4-octylphenyl crotonate and 2,4-dinitro-6-octylphenyl crotonate |
| Dodine | n-dodecylguanidine acetate |
| Endosulfan | 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide |
| Ethion | O,O,O',O'-tetraethyl S,S'-methylene bis(phosphorodithioate) |
| Fluorodifen | p-nitrophenyl α,α,α-trifluoro-2,6-dinitro-p-tolyl ether |
| Hexachlorobenzene (HCB) | hexachlorobenzene |
| Hexachlorophene | 2,2'-methylenebis(3,4,6-trichlorophenol) |
| Methoxychlor | 1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane |
| Nitrofen (TOK®) | 2,4-dichlorophenyl p-nitrophenyl ether |
| Pentachlorophenol (PCP) | pentachlorophenol |
| Propanil | 3',4'-dichloropropionanilide |
| Pyrazon (Chloridazon) | 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone |
| Tetradifon | 4-chlorophenyl 2,4,5,4'-tetrachlorophenyl sulfone |
| **Polychlorinated Biphenyls (PCBs):** | Mixtures of chlorinated biphenyl compounds having various percentages of chlorination. |
| **Polychlorodibenzo-p-dioxins:** | Dibenzo-p-dioxins having any of the positions of chlorination such as the 2,3,7,8-, 1,2,3,7,8-, or octachloro- positions, present as contaminants in pesticide formulations containing phenols and their derivatives (2,4,5-T). |

- Chemical names are in accordance with Chem. Abstracts.
- Report individual isomers where possible.
- Some compounds have similar names but differ in the position or in certain regions rather than readily-evident features; for example, the herbicides 2,4-D and picloram are used mainly on sugar cane and rice, respectively.
- Name that appears in parentheses is considered to be a synonym.
- Name that appears in brackets is also acceptable, although not considered to be preferable; however, are of special interest in monitoring studies.

/ Schechter, 1973.[19]

MONS 039248

APPENDIX II-F

[10] Schechter, M. S. (1971), Revised chemicals monitoring guide for the National Pesticide Monitoring Program Journal. Vol. 5, No. 1, p. 60-71.

MONS 039249