SECTION III

FRESHWATER AQUATIC LIFE AND WILDLIFE

LISTINGS

PHTHALATES > "TOXIC SUBSTANCES"
PCB

DETERGENTS > "OTHER TOXICANTS"

MONS 039390

Freshwater aquatic life and wildlife

PHTHALATE ESTERS

The occurrence of dialkyl phthalate residues has been established in various segments of the aquatic environment of North America. Phthalate ester residues occur principally in samples of water, sediment, and aquatic organisms in industrial and heavily populated areas (Stalling 1972). In fish, di-n-butyl phthalate residues ranged from 0 to 500 µg/kg, and di-2-ethylhexyl phthalate residues were as high as 3,200 µg/kg. No well-documented information exists on the fate of phthalate compounds in aquatic environments.

Phthalate esters are widely used as plasticizers, particularly in polyvinyl chloride (PVC) plastics. The most common phthalate ester plasticizer is di-2-ethylhexyl phthalate. Di-n-butyl phthalate has been used as an insect repellant (Frear 1969) and in pesticide formulations to retard volatilization (Schoff and Mathis 1963). Production of dioctyl phthalate ester placticizers was estimated to be 4.10×10^8 lbs in 1970, (Neely 1970). Total phthalate ester production was reported to be 8.40×10^8 lbs in 1958, of which 4.40×10^8 lbs were dioctyl phthalate esters (Nematollahi, Gueser, and Autian 1967). Production of phthalic anhydride was estimated to be 7.60×10^8 lbs in 1970 (Neely 1970). PVC plastic formulations may contain 30 to 60 parts per hundred of phthalate ester plasticizer (Nematollahi, Gueser, and Autian 1967).

Studies to determine the acute or chronic toxicity effects of phthalate esters or other plasticizers on aquatic organisms have only been undertaken (Stalling 1972). For example, the acute toxicity of di-n-butyl phthalate to fish is extremely low compared to pesticides (Table III-14).

TABLE III-14

Acute Toxicity of Di-n-butyl Phthalate to Four Species of Fish and Daphnia Magna.

Species	Temperature	LC50 in µg/l 24 hr	48 hr	96 hr	
Fathead minnow (Pimephales promelas)	-	1490	1300	(Stalling)	
Bluegill (Lepomis macrochirus)	1230	731	731	(Stalling)	
Channel catfish (Ictalurus punctatus)	3720	2910	2910	(Stalling)	
Rainbow trout (Salmo gairdneri)	-	-	6470	(Sanders)	
Daphnia magna	-	-	>5000	(Sanders)	

Daphnia magna were exposed to 0.1 µg/l of ^{14}C di-n-butyl phthalate and the organisms accumulated chemical residues of 600 µg/kg within 10 days, or a 6,000-fold magnification (Sanders, unpublished data 1971). However, after transfer of the Daphnia to uncontaminated water, approximately 50 per cent of the di-n-butyl phthalate was excreted in three days. It was

recently found that a concentration of 3 µg/l of di-2-ethylhexyl phthalate significantly reduced (p = 0.01) the growth and reproduction of Daphnia magna (Sanders unpublished data 1971). 267

The acute toxicity of phthalate esters appears to be relatively insignificant, but these compounds may be detrimental to aquatic organisms at low chronic concentrations. The production of large amounts and the widespread use of phthalate ester plasticizers invariably contributes to the overall contamination of the aquatic environment. clean up

endation

Until a more detailed evaluation is made of toxicological effects of phthalate esters on aquatic ecosystems, a safety factor of 0.1 has been applied to data for Daphnia magna toxicity, and a level not to exceed 0.3 µg/l should protect fish and their food supply.

ORINATED 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; Holmes, Simmons, and Tatton 1967; Koeman et al. 1969; Risebrough et al. 1968). The environmental occurrence, uses, and present toxicological aspects of PCB were recently reviewed by Peakall and Lincer (1970), Gustafson (1970), Risebrough (1970), and Reynolds (1971).

Biphenyls may have one to 10 attached chlorine atoms, making possible over 200 compounds (Gustafson 1970). 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, Stalling in press).

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) and modified by Stalling and Huckins (1971). A method using separation on a charcoal column has shown good reproducibility (R. Frank and J. Rees, personal communication). 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 is in the range of 100 to 1,000 ug/l (Apgar and George 1970). 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).

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 (ug/g whole body) 1232	1248	1254	1260	Total
Ohio	Cincinnati, O.	Carp Cyprinus carpio	10	75	42	6.0	133
Ohio	Cincinnati, O.	White crappie Poximus annularus	16	17	27	5.6	66
Ohio	Marietta, O.	Channel catfish Ictalurus punctatus	38	23	11	4.9	77
Ohio	Marietta, O.	Channel catfish	16	5.2	13	4.6	38
Yazoo	Redwood, Miss.	Smallmouth buffalo Ictiobus bubalus	72	-	1.4	-	73
Hudson	Poughkeepsie, N.Y.	Goldfish Carassius aurratus	9	173	32	-	213
Allegheny	Natrona, Pa.	Walleye Stezostedion vitreum V.	-	5.2	25	4.6	35
Delaware	Camden, N.J.	White perch Roccus americanus	-	8.0	6.8	3.9	19
Cape Fear	Elizabeth Town, N.C.	Gizzard shad Porosoma cepedianum	19	-	2.6	1.1	23
Lake Ontario	Port Ontario, N.Y.	White perch	13	-	4.6	1.2	19
Mississippi	Memphis, Tenn.	Drum Aplodinotus grunniens	11	-	4.5	3.4	19
Merrimac	Lowell, Mass.	Drum	14	75	6.1	3.2	98

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The Monsanto Company, the sole manufacturer of PCB in the United States (Gustafson 1970), markets eight formulations of chlorinated biphenyls under the trademarks Aroclor® 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268. The last two digits of each formulation designate the per cent chlorine. Aroclor® 1248 and 1254 are produced in greatest quantities. They are used as dielectric fluids in capacitors and in closed-system heat exchangers (Papageorge and George 1970). Aroclor® 1242 is used as a hydraulic fluid, and Aroclor® 1260 as a plasticiser. Chlorinated terphenyls are marketed under the trademark Aroclor® 5442 and 5460, and a mixture of bi- and terphenyls is designated Aroclor® 4465. The isomer composition and chromatographic characteristics of each formulation have been described by Stalling and Huckins (1971) and Bagley, Reichel, and Cromartie (1970). A contaminant of some PCB, especially those manufactured in Europe, are chlorinated dibenzofurans (Brungs, personal communication 1972). While these by-products 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 is the apparent toxicity of PCB to fish (Mayer, in press). 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 as it has to fish. In 4- and 7-day tests (Saunders, in press), 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 is an extreme range in the reported short-term lethal levels of Aroclor® 1254 for invertebrates. Saunders (in press) reported a 96-hour LC50 as 80 µg/l for crayfish and only 3 µg/l for glass shrimp (Paleomonetes) in 7-day tests; and Duke, Lowe, and Wilson, Jr. (1970) reported that as little as 0.94 µg/l killed immature pink shrimp (Panaeus duorarum). Part of this variation is related to exposure periods in the tests; part is no doubt the variation in species response. Again this emphasizes the point that short-term tests of acute toxicities of PCB have serious limitations.

Marine animals may be more easily killed by PCB than freshwater (see the Panel report on Marine Aquatic life and Wildlife, Section IV). When two estuarine fishes (Lagodon rhomboides and Leiostomus xanthurus) were exposed for 14 to 45 days to Aroclor® 1254, mortalities were observed at 5 ppb (Hanson, et al. 1971). This indicated a toxicity about five times greater than summarized above for freshwater fish, but about the same as the toxicity for the marine crustaceans mentioned above.

Feeding Studies

Dietary exposure to PCB seems to be less of a direct hazard to fish than exposure in water. Coho salmon (Oncorhynchus kisutch) fed Aroclor® 1254 in varying amounts up to 14,500 µg/kg body weight per day accumulated whole body residues which were only 0.9 to 0.5 of the level in the food after 240 days of dietary exposure. Growth rates were not affected. However, all fish exposed to the highest treatment died after 240 days exposure; and thyroid activity was stimulated in all except the group treated at the lowest concentration (Mehrle and Grant, unpublished data 1971).

At present evaluation of data from laboratory experiments indicates that exposures to PCB in water represents a greater hazard to fish than dietary exposures. However, in the environment, residue accumulation from dietary sources could be more important because since PCB have a high affinity for sediments, and therefore, they readily enter food chains (Duke, Lowe, and Wilson 1970; Nimmo, et al. 1971).

ues in Tissue

It is clear that widespread pollution of major waterways has occurred and that appreciable PCB residues exist in fish. When analyses of 40 fish from the 1970 National Pesticide Monitoring Program were made, only one of the fish was found to contain less than 1 µg/g PCB (Stalling and Mayer 1972). The 10 highest residue levels in the 40 selected fish ranged from 19 µg/g to 213 µg/g whole body weight.

By contrast, residues measured in ocean fish have been generally below 1 µg/g (Risebrough 1970; Jensen, et al. 1969). Between the ranges in freshwater fish and those in marine fish are the levels of PCB found in seals (Jensen. et al. 1969; Holden 1970), and in the eggs of fish-eating birds in North America (Anderson et al. 1969; Reynolds 1971; Mulhern et al. 1971).

In laboratory experiments crustacea exposed to varying levels of Aroclor® 1254 in the water concentrate the PCB within their bodies more than 20,000 times. The tissue residues may sometimes reach an equilibrium, and in Gammarus fasciatus PCB did not concentrate beyond 27,000 times despite an

additional 3-week exposure to 1.6 µg/l Aroclor® (Saunders 1972). 388

In contrast, PCB residues in crayfish did not reach equilibrium after a 28-day exposure. PCB concentration factors by two estuarine fishes, Lagodon rhomboides and Leiostomus xanthurus, were similar to that described for crustaceans, i.e., about 10,000 to 50,000 times the exposure levels in water (Hansen et al. 1971). 373 It is important to note that these accumulations occured at water concentrations of PCB that killed the fish in 15 to 45 days.

Also similar were the accumulation ratios of 26,000 to 56,000 for bluegills (Lepomis macrochirus) chronically exposed to 2.15 µg/l of Aroclor® 1248 and 1254. Fathead minnows (Pimephales promelas) chronically exposed to Aroclor® 1242 and 1254 for 8 weeks concentrated PCB's 100,000 and 200,000 times the exposure levels, respectively. Residues of 50 µg/l (whole body) resulted from exposure for 8 weeks to 0.3 µg/l Aroclor® 1254. These experiments with bluegills also indicated that the maximum levels of PCB were generally related to the concentration of PCB in the water (50,000 - 200,000 times higher) to which they were exposed (Stalling and Huckins, unpublished data, 1971). 397

Effects on Reproduction

PCB residues in salmon eggs are apparently related to mortality of eggs. In preliminary investigations in Sweden, Jensen and his associates (1970) reported that when residues in groups of eggs ranged from 0.4 to 1.9 µg/g on a whole weight basis (7.7 to 34 µg/g on a fat basis), related mortalities ranged from 16 per cent up to 100 per cent.

PCB concentrations in the range of 5 to 10 µg/l in water interfered with reproduction of several aquatic animals according to recent work of Nebeker, et al., Puglisi, and DeFoe (1971). 381 About 5 µg/l of Aroclor® 1248 was the highest

concentration that did not affect reproduction of Daphnia magna and Gammarus. True Pseudolimnaeus. In tests of reproduction by fathead minnows (Pimephales promelas) all died when exposed chronically to greater than 0.3 µg/l of either Aroclor® 1242 or Aroclor® 1254. Reproduction occurred at and below this same concentration of Aroclor® 1242, and at and below 2.8 µg/l of Aroclor® 1254.

The association between residue levels and biological effects in aquatic animals is scarcely known, but the work of Jensen, Johansson, et al. Olsson (1970) 377/ suggested that about 0.5 µg/g of PCB in whole salmon eggs might be the threshold for egg mortality. Such a level in eggs would be associated with levels in general body tissue (e.g., muscle) of 2.5 to 5.0 µg/g. The residue in muscle corresponded to the present Food and Drug Administration level for allowable levels of PCB in fish used as human food. Residues measured in the survey by the 1970 National Pesticide Monitoring Program were generally above 5 µg/g.

Applying a minimal safety factor of 10 for protection of the affected population, and for protection of other species higher in the food chain, would yield a maximum permissible tissue concentration of 0.5 µg/g in any aquatic organism in any habitat affected by PCB.

General Considerations and Further Needs

Another means of control would be justified in view of the toxicity of PCB, the lack of knowledge about how it first enters natural ecosystems as a pollutant, and its apparent distribution in high concentrations in freshwater fish in the United States. This method would be to regulate the manufacture of PCB and maintain close control of its uses to avoid situations where PCB is lost to the environment. The Monsanto Company recently restricted the sale of PCB for uses in which disposal of the end products could not be controlled, as with plasticizers (Gustafson,

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Basis for Recommendations

For PCB levels in water, the most sensitive reaction shown by aquatic organisms is to the lethal effects of low concentrations continually present in water for long periods (weeks or months). Concentrations in the range of 1 to 8 µg/l have been shown to be lethal to several animals. The work of Hansen, et al. (1971) and Stalling and Huckings (unpublished data, 1971) indicates that concentrations of 0.01 µg/l of PCB in water over periods of up to 36 weeks could lead to dangerous levels of PCB in the tissues of aquatic organisms. Accumulation by factors of 75,000 to 200,000 times is indicated by their work. If the higher ratio is taken, 0.01 µg/l in water might result in 2.0 µg/g in flesh on whole fish basis. This is comparable to the residue level in salmon eggs associated with complete mortality of embryos. Therefore, a concentration is recommended that is reduced by a factor of 5, or 0.002 µg/l. In addition, a control based on residue levels is required, as well as one based on PCB in the water.

Recommendations

Aquatic life should be protected where the maximum concentration of total PCB in unfiltered water does not exceed 0.002 µg/l at any time or place, and the residues in general body tissues of any aquatic organism do not exceed 0.5 µg/g.

Detergents

Detergents are a common component of sewage and industrial effluents derived in largest amounts from household cleaning agents. In 1965 a shift from tetrapropylene-derived alkylbenzene sulfonates (ABS) to the more biodegradable linear alkylate sulfonates (LAS) was made by the detergent industry. In current detergent formulas, LAS is the primary toxic active compound, two to four times more toxic than ABS. (Pickering 1966). However, toxicity of LAS disappears along with the methylene blue active substances (MBAS) response upon biodegradation (Swisher 1967). Retrieval of MBAS data from National Surveillance Stations throughout the U.S. from 1966 to the present showed that the mean of 3,608 samples was less than 0.1 mg/l. There has been a downward trend in MBAS concentrations. Only four stations reported mean concentrations greater than 0.2 mg/l.

The MBAS determination has been the routine analytical method for measurement of surfactant concentrations. Positive errors are more common than negative ones in the determination of anionic surfactants in water (Standard Method 1971). An infrared determination or a carbon absorption cleanup procedure is recommended when high MBAS concentrations are found.

Marchetti (1965) critically reviewed the effects of detergents on aquatic life. Most available information on LAS toxicity relates to fish. Short term studies by a number of investigators have shown that lethal concentrations to selected fish species vary from 0.2 to 10.0 mg/l (Hanson and Smith 1971). Bardach, Fujiya, and Holl (1965) reported

at 10 mg/l is lethal to bullheads (Ictalurus sp.), and that 0.5 mg/l eroded per cent of their taste buds within 24 days. Thatcher and Santner (1966) 536 ed 96-hour LC50 values from 3.3 to 6.4 mg/l for five species of fish.

535 Pickering and Thatcher (1970) found in their study of chronic city that a concentration of 0.63 mg/l had no measurable effect on the s cycle of the fathead minnow (Pimephales promelas), while a concentra- of 1.2 mg/l was lethal to the newly hatched fry. A safe level should between 14 and 28 per cent of the 96-hour LC50. Hokanson and Smith (1971) 532 rted that a concentration of 1 mg/l was an approximate safe concentra- for bluegills in Mississippi River water of good quality. Arthur (1970) 533 d that the no-effect level of LAS on Gammarus pseudolimnaeus was 0.2 .4 mg/l. This investigator also subjected opculate and pulmonate ls to 60-week exposures of LAS and showed the toxicity levels to be to 1.0 mg/l and greater than 4.4 mg/l, respectively.

Detergent Builders

Phosphates have been included in household detergents to increase their effectiveness, although this use has been seriously questioned recently. Nitrilotriacetate (NTA) and other builders have been tried, but most are either less effective or have been barred for reasons of potential health hazard. Available builders do not have serious direct effects on fish

aquatic organisms at concentrations likely to be encountered in receiving waters. In view of the uncertain legal status of present commercial detergents and the extensive search for adequate substitutes now in progress, recommendations for builders is not practical at this time. However, it can be stated that a satisfactory builder should be biologically degradable and nontoxic to aquatic organisms and humans and that it should not cause aesthetic problems in the receiving water.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of LAS safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.05; but no concentration greater than 0.2 mg/l is recommended at any time or place.

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