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APPENDIX A

ANNUAL REPORT
OF THE
WATER QUALITY OBJECTIVES SUBCOMMITTEE
TO THE
IMPLEMENTATION COMMITTEE AND
GREAT LAKES WATER QUALITY BOARD

WATER QUALITY OBJECTIVES FOR THE GREAT LAKES

JUNE 1975

DSW 345896

STLCOPCB4084359

TOXIC SUBSTANCES - PERSISTENT COMPOUNDS

PERSISTENT ORGANIC CONTAMINANTS

WE SHOULD IDENTIFY WHO WROTE ORGAN & date

RECOMMENDATION

It is recommended that the following numerical objectives for persistent organic contaminants be adopted to replace the existing interim objectve in Annex I, paragraph 2 (c) of the Water Quality Agreement:

Persistent organic contaminants should nowhere in the Great Lakes system exceed the water and tissue concentrations specified below for the protection of aquatic organisms and consumers of fish.

permeable & what procedure

Compounds	Specified concentrations: Water (ug/l)	Tissue ug/g
Phthalate esters		
Dibutyl phthalate	4.0	U*
Di-(2- ethylhexyl phthalate	0.6	U*
Other phthalate esters	0.2#	U*
Total P.C.B.'s	U*	0.1
Total D.D.T./D.D.E.	.003#	1.0
Total Aldrin/Dieldrin	.001#	0.3+
Total Heptachlor/Heptachlor epoxide	.001#	0.3+
Endrin	.002#	0.3+
Toxaphene	.008	U*
Chlordane	.060	U*
Lindane	.010	0.3+
Methoxychlor	.040	U*

U - undetermined at present*

 # - recommended quantification limit

+ - based upon U.S.F.D.A. guidelines for edible portions of fish.

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For other organic contaminants, the concentrations of which are not specified but which can be demonstrated to be persistent and are likely to be toxic, it is recommended that the concentrations of such compounds in water or aquatic organisms be limited to the detection level as determined by the best scientific methodology available at the time.

Note: Such a compound for which concentrations cannot be specified is Mirex, a rationale for which appears along with those for compounds specified above.

Note: Where waters are found to be contaminated as defined by exceeding the appropriate objective, all reasonable and practicable measures should be taken by the regulating agencies to reduce the input of the persistent organic contaminant to any part of the Great Lakes system.

EXISTING OBJECTIVE:

The recommended numerical objectives are intended to replace the existing interim objective in Annex 1, paragraph 2 (c) of the Agreement which states:

> "Persistent Organic Contaminants. Persistent pest control products and other persistent organic contaminants that are toxic or harmful to human, animal or aquatic life should be substantially absent in the waters."

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RATIONALE

Introduction

Synthetic organic contaminants entering surface waters may be broadly divided into persistent and non-persistent compounds. The distinction is important since the organic

contaminants known to present the greatest hazard to human, animal and aquatic life are those which are resistant to degradation and which are thus available for dispersion in the environment and for incorporation into biological tissues. Concentrations of persistent organic contaminants in the aquatic environment seldom achieve acutely-toxic proportions except in localized situations due to accident or misuse. Of much greater concern are effects due to long-term exposure at sub-lethal levels and bio-concentration of residues resulting in tissue accumulations of increasing magnitude with each higher level in the aquatic food chain. For these reasons it is necessary to consider persistent contaminants separately from those which are readily decomposed to non-toxic constituents.

Persistent organic contaminants are, according to the Canada-U.S. Agreement, to be "substantially absent" from Great Lakes waters. While the Water Quality Objectives Subcommittee would like to interpret this as completely absent from the aquatic ecoysystem, it is constrained by the need to justify selected levels based upon protection of all potential uses. Consequently, it recommends levels based upon (1)protection of all aspects of aquatic life and human health as measured by water and tissue levels, (2) quantification limits for water concentrations, and (3) drinking water and food standards when these levels are limiting. Recreational effects of persistent organic compounds in water, with the possible exception of oil (covered under a separate objective), do not present any limitations to the introduction of such material into the water system. Agricultural use levels also are not likely to provide adequate protection for aquatic life.

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PERSISTENCE

A persistent compound is defined as one which either (a) by itself or as its transformation product, has a half-life for degradation under natural environmental conditions of more than eight weeks, or, (b) by itself or as its transformation product, on entering surface waters may bioconcentrate in the biota of the receiving system.

Persistence is the property of chemical compounds, measured in units of time, which describes their ability to resist structural alteration under specific physical and chemical conditions. Under similar environmental conditions, different compounds exhibit different persistences depending on their molecular configuration. No standard test of persistence has yet been developed and, consequently, the term lacks precise definition. This is reflected in the common practice of arbitrarily classifying environmental contaminants as persistent when their presence can be demonstrated in different substrates several days or weeks after release.

The development of a standard test of persistence is a desirable precursor to the introduction of an objective for persistent contaminants in water. However, such a test cannot be arbitrarily selected, will require careful research and evaluation, and must be generally acceptable to the scientific community before its application for regulatory purposes. Whereas such research should be stimulated at the earliest opportunity, there is no possibility that an acceptable test for 'persistence' can be developed for incorporation into the impending revision of the U.S.-Canada Agreement on the Great Lakes' Water Quality. Thus, if the word 'persistence' is to appear in the objectives it must include the present broad meaning indicated in (a) of the above definition.

A laboratory study of eight organochlorine, ten organophosphorus and seven carbamate compounds showed marked differences

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in persistence in river water over an eight week period (Eichelberger and Lichtenberg, 1971). The results indicated, however, that 50% or more of the initial concentrations (10 ug/l) of all major environmental contaminants studied remained at the termination of the study. Thus a half-life of eight weeks would appear to be a reasonable criterion for the separation of persistent and non-persistent compounds in water.

In keeping with the intent of the objectives that persistent organic contaminants be substantially absent, the definition has been modified to include the property of bioconcentration potential so as to provide for the distinct possibility that levels in tissue may accumulate from water concentrations below those which can be detected. This effect is provided for in part (b) of the definition.

While the problem of bioconcentration is real and is the reason for the inclusion of tissue levels in the objectives, bioconcentration factors are not standardized, sometimes combining dietary and direct water uptake, and sometimes being acquired from systems considerably above the solubility of the compound under examination. As a consequence of these, and other difficulties in determining this factor, no defensible objective can presently be made based primarily upon this influence. It is hoped that future work in this area may allow the situation to change.

Aquatic Life

Body burdens of persistent organic contaminants in aquatic biota and those of their predators may become limiting for species survival. Most of such compounds are classified by organic chemists as "non-polar" and as such they are very insoluble and are liable to occur predominantly as adsorbed

material on the particulate load. From there it may be ingested along with the particulates, thus entering the food chain, or it may be deposited in the sediment from where it can enter via benthic organism. Fish may also absorb these compounds directly through the gills. In higher trophic organisms, the persistent material usually ends up in the liver or in the adipose tissue due to its preferential solubility in fats and oils over that in aqueous fluides. In many cases, bioconcentration occurs as well since the material then may not readily be excreted by the organism. As a consequence of these considerations, sediments, plankton, fish tissue and predators of fish are probably better indicators of the presence of persistent organic contaminants than is water. Predators are of concern since avian and other non-aquatic predators feed on aquatic life and their body burdens may accumulate to toxic levels as a result. Since fish are the food source of concern for these predators, levels are largely set for fish tissue, but where it can be shown that detrimental effects occur in the predators the tissue level objective should be extended to include the predators.

The dynamics of adsorption also give rise to increased levels of persistent organic contaminants in the sediments. However, sediments are prone to movements over large distances through current action and additionally, present technology does not permit the determination of their deposition rates on a useful time scale for these monitoring purposes. Hence, they presently can only give indications of the presence of the contaminants but cannot easily be related to detrimental effects. It is recommended that studies be undertaken into such sampling methods as would permit the use of sediment levels for measuring contamination but for the present, criteria are not recommended for this compartment of the ecosystem.

Specific recommendations have been made for those cases where significant studies have determined "safe" levels for representative fish and invertebrate species by chronic toxicity experiments. In cases where subtle and deleterious effects were noted at the lowest chronic dose level (e.g. a partial reduction in hatchability of eggs), an arbitrary safety factory of 0.2 was applied to estimate the "safe" level. In cases where the acute toxicity studies indicated that some species of fish were more sensitive than those actually investigated, an experimentally determined application factor for fish for the compound in question was utilized to estimate a "safe" level for the more sensitive species of fish. Data for invertebrate studies were handled in the same fashion.

When chronic field studies were available which documented water concentrations and used intensive ecological analyses, these were given greater weight than laboratory studies. Concentration factors for pesticides from water to aquatic life were found to be too variable (often greater than an order of magnitude) to utilize meaningfully in the establishment of water quality criteria. Therefore, body burdens of various persistent chemicals in fish were utilized directly, when appropriate information existed. Protection of wildlife which consumes aquatic life, is based on chronic feeding studies of sensitive species and calls for restrictions on body burdens.

It is the intent of the Agreement to protect boundary waters of the Great Lakes System as a raw public water supply which will produce a safe drinking water after treatment. In addition, the use of fish for human consumption should be protected. Existing standards for most of the toxic persistent

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organic contaminants are inadequate to protect aquatic life. Protection of fish as a resource is provided by quidelines of the U.S.F.D.A. for three persistent organics. (See recommendations). As new standards related to raw water supplies or drinking water which are lower than recommended water concentrations are developed and adopted by Canadian or U.S. federal agencies. They should be adopted as part of the specific objectives, as should new edible tissue guidelines from U.S. Food and Drug Administration or the Canadian Food and Drug Directorate.

QUANTIFICATION LIMITS

The water quality objectives proposed for persistent organic contaminants have been based on the intent expressed within the existing Agreemtn which is that such materials should be "substantially absent" within the boundary waters of the Great Lakes. The assumed philosophy, which is perpetuated here, is that danger exists in allowing persistent materials of unknown fate or biological significance to be added to surface waters within arbitrarily established limits because there is no assurance that bioconcentration will not occur and reach unacceptable levels. Corrective action may come too late to offset serious enviornmental consequences. Therefore, the philosophy of substantial absence of these substances is endorsed. In a practical sence, this is that concentration which is below that which can be quantified. That such quantification limits should be the objective for compounds without "safe levels is indicated in the preceeding, but it should be particularly so for proven carcinogens. In a survey of some ten laboratories in the Great Lakes region which are currently doing routine determinations of pesticides and other persistent organic contaminants, the following means and ranges of quantification limits were reported.

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Table 1 - Persistent Organic Contaminants Quantification Limits.

Compound	Mean ug/l	Range ug/l	Recommended quantification limit ug/l
Lindane	.004	.001-.010	.001
Heptachlor	.004	.001-.010	.001
Heptachlor Epoxide	.004	.001-.010	.001
pp'-DDD	.012	.001-.050	.002
pp'-DDE	.011	.001-.050	.002
pp'-DDT	.011	.001-.125	.003
op'-DDT	.014	.001-.045	.003
Aldrin	.004	.001-.010	.001
Dieldrin	.008	.001-.025	.001
Endrin	.008	.001-.020	.002
Chlordane	.005	.002-.010	.002
Total PCB	.035#	.020-.100#	.010
pp' Methoxychlor	.020	.010-.050	.010
Phthalate esters	.6	.1 -1.5	.2

\# does not include a single high value of 1.5 ug/l.

* the mean of the lowest three values reported.

The third column is the mean of the lowest three quantification limits reported. Since it is desired to provide incentive to the development of more sensitive procedures, and not to condone insensitive determinations, it is these means which are recommended. They are employed, where appropriate, for specification of concentrations for which experimental data are not available to produce "safe" water levels but where there are data to establish "safe" tissue levels.

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Where an organic compound can be demonstrated to be persistent and likely to be toxic and for which data are unavailable to establish either "safe" water or tissue concentrations, it is recommended that its concentration in water or aquatic organisms be limited to the detection level as determined by the best scientific methodology available at the time.

These quantification and detection limits, however, should not be accepted as permanent substitutes for experimentally determined "safe" concentration - rather it is intended that they should stimulate research on safety evaluations and analytical methods, plus provide a mechanism for action in the case of newly observed contaminants.

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PERSISTENT ORGANIC CONTAMINANTS

POLYCHLORINATED BIPHENYLS

RECOMMENDATION

It is recommended that the following new objective for polychlorinated biphenyls be adopted:

"The concentration of total polychlorinated biphenyls in fish tissues (whole fish, calculated on a wet weight basis), should not exceed 0.1 micrograms per gram for the protection of fish consuming birds and mammals.

Note: The Subcommittee expresses concern that a water concentration objective for this ubiquitous contaminant is unavailable. Based upon poorly defined bio-concentration factors it may be concluded that PCB's in water should not exceed 0.001 micrograms per litre. However, this level may not be adequate to provide protection to certain predators, and could presently not be enforced because of insufficiently sensitive quantification limits.

RATIONALE

Introduction

In North America polychlorinated biphenyls (PCB's) are manufactured solely by the Monsanto Chemical Company and are distributed under the trade name AROCLOR^{R}. Each Aroclor is a mixture of various isomers of which 210 may occur in theory, the actual number of isomers formed chemically is probably closer to 100. In addition, a significant percentage of these isomers has been predicted to exist in pairs of optically active forms (Kaiser, 1974).

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Polychlorinated biphenyls are now known to constitute the third most widely distributed pollutants on Earth, exceeded only by the chlorinated insecticides DDT and dieldrin. Similar to the latter compounds, PCB residues are found in the fat deposits of numerous warm and cold-blooded animals including Man. Their persistance is generally considered to be greater than most chlorinated insecticides. In the aquatic environment, PCB's have been detected in water, sediments, invertebrates, fish and waterfowl with highest levels being recorded in predatory organisms high in the food chain. While greater quantities are found in areas close to heavy industrialization, substantial residues have been detected in fish from undeveloped localities suggesting that aerial transport may play a significant role in their distribution.

PCB's In Great Lakes Waters

Contamination of the Great Lakes by PCB's has been, and continues to be, extensive. Fifty-seven per cent of water samples from 30 major tributaries analyzed by Michigan Water Resources Commission (1971) contained detectable concentrations of PCB (0.01 ug/l). Mean values determined for Michigan tributaries of Lakes Michigan, Huron, Superior, St. Clair and Erie were .023 ug/l, .228 ug/l, .010 ug/l, .081 ug/l, and .186 ug/l total PCB respectively. The Canada Centre for Inland Waters examined open waters of Lakes Ontario and Erie during 1971 and measurable quantities were found in 60 percent and 63 percent of the samples respectively. Summaries of data from the three basins in each lake are presented in the Report of the IJC Boards to the IJC (1972). The highest mean value was 0.062 ug/l for bottom waters of Lake Ontario (western region), while the lowest was .012 ug/l for

the surface of Lake Ontario (eastern region). Lakewide means for surface and bottom samples were .030 µg/l and .032 µg/l respectively for Lake Ontario, and .027 µg/l and .025 µg/l for Lake Erie. Samples taken from Hamilton Harbour (Lake Ontario) by the Ontario Ministry of Environment in 1972 showed ranges of PCB's in water of .035 -.095 µg/l and 0.2 - 10.1 µg/g in sediments (Berg et al., 1974)

PCB's In Biota

Fish contamination is also widespread. The U.S. Food and Drug Administration guideline of 5 µg /g in edible tissue has been exceeded in numerous species in Lake Michigan including lake trout, coho salmon, chinook salmon and chub. In Lake Huron, walleye, whitefish, and catfish are above the tolerance level and likewise smelt and coho salmon in Lake Ontario. PCB concentrations in Lake Erie fish are generally below 5 µg/g with the exception of white bass (Report of the IJC Boards to the IJC, 1972). Recent analyses by the Ontario Ministry of the Environment on fish from the St. Clair River revealed muscle concentrations of 4.3 - 12.3 µg/g in white bass, 0.1 - 6.8 µg/g in pike, 0.1 - 2.8 in white suckers and 1.5 - 4.7 µg/g in coho salmon. Perch from Lake St. Clair showed levels of 0.1 - 0.25 µg/g and in the same area walleye contained 0.2 - 3.0 µg/g (Berg et al., 1974).

A serious situation exists with respect to populations of fish eating birds in the vicinity of the lower Great Lakes. Severe reproductive failure has been identified in herring gull colonies around Lake Ontario. While eggshell thinning has been correlated with DDE content of the eggs there is a positive correlation between early embryonic

mortality and PCB contamination (Gilbertson and Fox, 1975). Geometric means for PCB's in eggs of four fish-eating bird species are given below (National Research Council Canada, Associate Committee on Scientific Criteria for Environmental Quality, 1974).

PCB RESIDUES IN BIRDS EGGS (ug/g, dry weight basis)

Location	Herring gull	Ring-billed gull	Common tern	Double-crested cormorant
Lake Nipigon				77.5(52)
Lake Huron	368(5)	113(2)	81.7(8)	140.0(55)
Detroit River	520(2)			
Lake Erie	300(6)	243(4)	156(15)	63.7(18)
Hamilton Harbour			258(71)	
Lake Ontario	565(16)	379(4)	268(20)	114(7)

The major effect of PCB's on young birds is to produce symptoms of chick edema disease. The symptoms are subcutaneous pericardial and abdominal edema, prophyria, liver necrosis and high mortality (Gilbertson, 1974; Gilbertson and Hale, 1974; Gilbertson and Fox, 1975). In herring gull chicks from Lake Ontario colonies poor hatching success is associated with these forms of edema, increased porphyrin synthesis but not liver necrosis. These signs were associated with levels of PCB's of over 900 ug/g on a dry matter basis in the liver - amongst the highest levels in the world. Less severe signs were seen in Lake Erie chicks at about 600 ug/g, but were not completely absent in a control group from outside the Great

Lakes at about 35 ug/g. Clearly, even the Lake Erie group is contaminated by more than an order of magnitude above these.

In summary there can be little doubt that the existing state of PCB contamination in the Great Lakes system is excessive. Of particular concern must be the higher forms of life in which the process of bioconcentration causes the greatest residues to be accumulated. At present, there are insufficient data to estimate water concentrations of PCB's which will assure protection of predatory fish, fish eating birds and other predators; this will require greater understanding of the correlation of dietary intakes and bioconcentration factors.

Effects of PCB's On Biota

PCB's are toxic to aquatic life by direct exposure and are hazardous also to consumers of contaminated fish. Reproduction of midges and Daphnia magna was reduced at 0.45 ug/l (Aroclor 1254) and 1.3 ug/l respectively (Nebeker and Puglisi, 1974). The highest concentration of Aroclor 1248 having no effect on the fathead minnow was about 0.3 ug/l (National Water Quality Laboratory, 1974), a concentration which resulted in tissue residues of about 90 ug/g or 18 times the guideline for human consumption recommended by U.S. and Canadian federal health authorities. This indicates a bioconcentration factor for fathead minnows of approximately 3×10^5. The factor for bluegills with Aroclors 1248 and 1254 has been estimated at 7.1×10^4 (Stalling and Mayer, Jr., 1972) while large Lake Michigan coho salmon have mean tissue levels of about 15 ug/g (Veith, 1973) which is 1.5×10^6 times greater than the maximum open water concentration of around 0.010 ug/l (Lake Michigan Toxic Substances Committee Report).

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Two ug/g PCB's in fish flesh has been shown to prevent survival of newborn commercial ranch mink (Ringer et al., 1972) while reproduction was eliminated in mink fed a beef diet containing 0.64 ug/g Aroclor 1254 (Platonow and Karstad, 1973). While this is not a subtle effect, it is the lowest dietary concentration observed to produce a deleterious biological effect. The safety factor of 0.2 applied to this results in the recommended tissue level of 0.1 ug/g.

The recommendation for PCB's is designed to protect the aquatic biota as well as the consumer of aquatic life. A conservative bioconcentration factor of 10^5 could be used to calculate a water concentration for total PCB's which should prevent tissue levels greater than 0.1 ug/g. This would result in a PCB concentration in water of less than 0.001 ug/l, a concentration which would be beyond the present routine analytical sensitivities and therefore impossible to monitor or enforce. It is therefore recommended that the regulatory agencies undertake fish and bird monitoring programs to determine compliance with the recommendation regarding tissue levels.

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