

QUANTITATIVE AQUATIC BIOLOGICAL INDICATORS

**Their Use to Monitor Trace Metal
and Organochlorine Pollution**

DAVID J. H. PHILLIPS

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and Organochlorine Pollution

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I also wish to express my appreciation to Professor Kenneth Mellanby and to Applied Science Publishers Ltd for their original suggestion that

such a book may be of interest to researchers at this time, and for their help in the production of the book itself.

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Lastly, I have dedicated the book to Dr Charles Boyden; those readers who knew him will understand my reasons.

Preface

The quantitation of pollutants in aquatic ecosystems is a relatively new research field. Much of the impetus for such research has been derived from tragedies such as at Minamata, and the minimisation of the detrimental effects of pollutants on humans is sufficient justification for such studies. However, there is little or no evidence to suggest that man is particularly susceptible to most pollutants compared to other organisms. I therefore envisage the monitoring of pollutants in aquatic ecosystems as a first step in the protection of the ecology of those ecosystems rather than as an inexpensive safeguard to man, although these aims are not mutually exclusive.

The use of biological indicator organisms to quantitate pollutants has essentially developed only during the last decade. It is undeniable that the technique is a powerful tool in our understanding of pollutant abundance and bio-availability in aquatic ecosystems. Most or all water bodies can be studied by this method, employing either indigenous or introduced species. Such monitoring will define the general abundance of specific pollutants in the study area, and may also be used to elucidate point sources of pollutants. There is no doubt that these techniques will eventually extend beyond the study of trace metals and organochlorines to petroleum hydrocarbons and other groups of major pollutants. However, the pitfalls in the use of biological indicator organisms to quantitate pollutant availability or abundance in water bodies are many; I have attempted to define most of these in this book, in an effort to aid researchers who wish to use such methods.

My reviews of the use of biological indicator organisms to quantitate trace metals and organochlorines, published in the journal *Environmental Pollution* in 1977 and 1978, served as a 'springboard' for the completion of this work. Professor Kenneth Mellanby first suggested to me in late 1978

that such a book might be a worthwhile project, as it became clear that the field was so broad that no journal review could cover all aspects completely. I have attempted to include all the aspects of major importance in this book, although I cannot pretend that the literature coverage is necessarily exhaustive throughout. Wherever possible, I have extended presently available data with cautious speculation and hypothesis. Further research is needed in almost every aspect of the use of biological indicators; if such speculation encourages further study, one aim of the book will have been satisfied.

The major intention of the book is, however, as an aid to refinement of the use of indicator organisms. If the correct sampling, analytical and interpretive techniques are employed, this method of monitoring provides rapid and inexpensive data which cannot be produced by any other type of study. I suggest that we need such data now, on a global scale, such that the process of improving water quality throughout the coastal and open ocean waters of the world may begin at once.

DAVID J. H. PHILLIPS

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CHAPTER I

Introduction: the Sources of Pollution

A. GENERAL

Pollution may be defined as a man-induced detrimental alteration to the ecosphere. In a sense, all organisms pollute their immediate environment, at least by the excretion of waste products. However, most organisms are rarely present at sufficient density to endanger their own viability by the excretion of wastes. By contrast, man excretes not only wastes derived from the breakdown of natural food products, but also expels toxic materials from his body, his factories and his cities. Whether the present global concern about man-induced pollution indicates a growing awareness that man is endangering his own viability and whether such an effect is due to the density of *Homo sapiens* or to the unusual ability of this organism to elicit massive and enduring alteration of the environment, are matters for conjecture.

This book is concerned with pollution of the aquatic environment by trace metals and organochlorines; areas of the greatest concern are dominated by anthropogenic inputs. Most of the published data considered herein for trace metals involve such elements as silver, arsenic, cadmium, cobalt, chromium, copper, iron, mercury, nickel, lead, selenium, tin and zinc. Occasionally, other elements (including radionuclides and trans-uranics) will be referred to, although the present work does not in any way pretend to cover these more esoteric elements completely. All such elements will be referred to collectively as trace metals, although this may be considered a misnomer in some cases. The organochlorines considered include the pesticide DDT and its metabolites DDE and DDD, methoxychlor, aldrin, dieldrin, endrin, heptachlor and its epoxide, and BHC (including γ -BHC, also known as lindane). In addition to these pesticides, the non-pesticide polychlorinated biphenyls (PCBs) will also be

TABLE 1

CHEMICAL IDENTITIES OF ORGANOCHLORINES AND OTHER PESTICIDES REFERRED TO IN THE PRESENT REVIEW

Common name	Chemical name
Aldrin	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, <i>endo-exo</i> isomer
BHC	Cyclohexane, 1,2,3,4,5,6,-hexachloro-
Chlordane	4:7-Methanoindan, 1,2,4,5,6,7,8,8a-octachloro-3a,4,7,7a-tetrahydro-, <i>endo</i> -isomer
DDD	Ethane, 1,1-dichloro-2,2-bis (<i>p</i> -chlorophenyl)-
DDE	Ethylene, 1,1-dichloro-2,2-bis (<i>p</i> -chlorophenyl)-
DDT	Ethane, 1,1,1-trichloro-2,2-bis (<i>p</i> -chlorophenyl)-
Dieldrin	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-, <i>endo-exo</i> isomer
Endosulfan	5-Norbornene-2,3-dimethanol-, 1,4,5,6,7,7-hexachloro-, cyclic sulphite
Endrin	1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-, <i>endo-endo</i> isomer
Heptachlor	4:7-Methanoindene, 1,4,5,6,7,8,8a-heptachloro-3a,4,7,7a-tetrahydro-, <i>endo</i> -isomer
Heptachlor expoxide	4:7-Methanoindan, 1,4,5,6,7,8,8a-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-, <i>endo</i> -isomer
Lindane	<i>Gamma</i> isomer of BHC (see BHC above)
Methoxychlor	Ethane, 1,1,1-trichloro-2,2-bis (<i>p</i> -methoxyphenyl)-
Mirex	1,3,4-Metheno-2 <i>H</i> -cyclobuta (<i>cd</i>)pentalene, dodecachloro-octahydro-
Parathion	Phosphorothioic acid, <i>O,O</i> -diethyl <i>O-p</i> -nitrophenyl ester
Propanil	Propionanilide, 3',4'-dichloro-
Sevin	Carbamic acid, methyl-, 1-naphthyl ester
Solan	<i>p</i> -Valeroloulidide, 3'-chloro-2-methyl-
Temefos (Abate)	<i>O,O,O',O'</i> -Tetramethyl, <i>O,O</i> -thiodi- <i>p</i> -phenylene phosphorothioate
Toxaphene	Chlorinated camphene containing 67-69 per cent chlorine

referred to; these compounds are used exclusively in industrial processes and exhibit remarkably similar ecosystem cycling (and pollution potential) to DDT and its metabolites (Peakall and Lincer, 1970).

All organochlorines referred to will be given their most common names throughout the text, some of which are trade names. The chemical names of each of these compounds are listed in Table 1 and structures of the most important compounds are shown in Fig. 1. The principal primary metabolites of DDT (1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethylene and 1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethane) will be termed DDE and

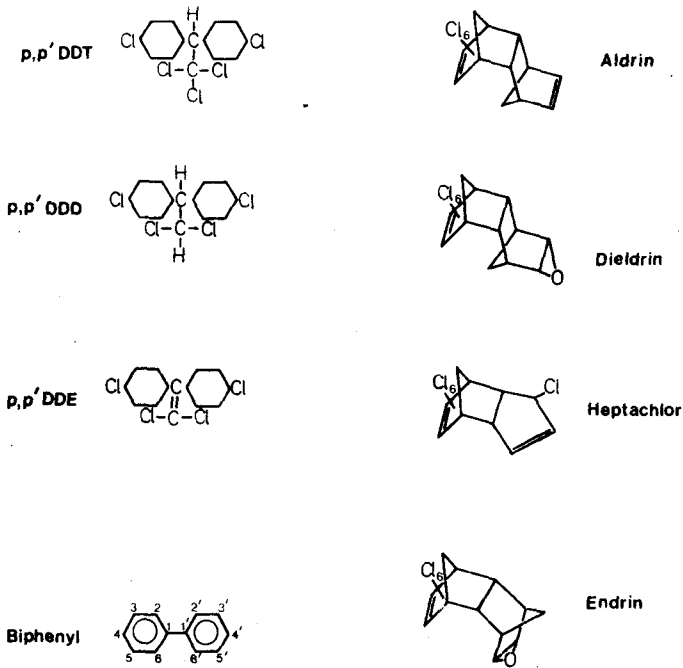


FIG. 1. Chemical structures of p,p' DDT and its major metabolites, and of aldrin, dieldrin, heptachlor and endrin. Also shown is the structure of the biphenyl ring on which PCBs are based.

DDD throughout and where any of these notations are used they refer to the p,p' isomers unless specifically stated otherwise. Some authors have reported data concerning the total concentration of DDT and its metabolites (DDT + DDE + DDD), without discriminating between the different compounds; the notation Σ DDT will be used throughout to refer to this combination. By contrast, the total amount of DDT in an organism will be referred to as whole-body DDT (where DDT alone is concerned) or whole-body Σ DDT (where the total concentration of DDT and its metabolites was measured). The annotation PCB will be used where authors have considered all polychlorinated biphenyls as a single group of compounds (adding peak heights to produce a total PCB concentration); if individual component PCBs were quantitated by authors, these will be referred to by use of their chemical names.

The emphasis of this review on the quantitation of trace metals and

organochlorines in biota—and the corresponding lack of discussion of other environmentally hazardous chemicals such as herbicides or organophosphates—is a result of the greater threat of the former chemicals to the well-being of aquatic ecosystems. Thus, whilst not wishing to diminish the importance of other pollutants, the trace metals and organochlorines are considered, by virtue of their extremely high toxicities and persistence in aquatic biota, as those contaminants most likely to elicit serious perturbation of the delicately balanced structure of aquatic food webs.

B. INPUTS OF TRACE METALS AND ORGANOCHLORINES TO AQUATIC ENVIRONMENTS

Table 2 shows the effects of man on the mobilisation rates of trace metals from the crust of the earth. The mining of metals by man is increasing the mobilisation of most elements enormously over that achieved by natural geological weathering. Thus, zinc and copper (both of which are extremely toxic in marine and freshwater environments) are being mined and

TABLE 2

THE EFFECTS OF MAN ON THE MOBILISATION RATES OF TRACE METALS. GEOLOGICAL RATES OF METAL MOBILISATION ARE COMPUTED FROM ANNUAL RIVER DISCHARGES TO OCEANS

Element	Geological rate ^a (10 ³ metric tons/year)	Man-induced rate (mining) (10 ³ metric tons/year)	Total in oceans ^c (10 ⁶ metric tons)	
Iron	25 000	319 000 ^a	395 000 ^b	4 110
Manganese	440	1 600	8 150	2 740
Copper	375	4 460	6 000	4 110
Zinc	370	3 930	5 320	6 850
Nickel	300	358	481	2 740
Lead	180	2 330	3 200	41
Molybdenum	13	57	74	13 700
Silver	5	7	9	137
Mercury	3	7	10.5	68
Tin	1.5	166	227	14
Antimony	1.3	40	65	274
Cadmium	No data	No data	17	68

^a Study of Critical Environmental Problems, MIT, 1970.

^b US Bureau of Mines, Minerals Yearbook for 1970.

^c From Bryan (1976); volume of oceans taken as 1.37×10^{21} litres.

mobilised at rates over ten times those expected from simple geological processes of weathering. Other highly toxic metals such as mercury and silver are being produced at a slower rate, but their mobilisation rates by mining nevertheless exceed those achieved by natural forces. Obviously, not all the metals mined represent an immediate hazard to the aquatic environment, but the potential for change in the pollution of aquatic areas by metals is nevertheless extremely high in some cases. Table 2 also includes estimates of the amounts of metals in the world's oceans. The hazard caused by man's mobilisation of metals can be estimated by comparing the mining rate (presumably directly proportional to the industrial need for metals, which itself will vary approximately with the metal discharge to the oceans) with this metal content of the oceans. On this basis, metals such as lead, iron and tin appear to possess high pollution potential; zinc and copper present less of a threat, mercury and cadmium still less and nickel and molybdenum least of all. Such a ranking of metals on the basis of man's ability to alter the concentrations in the world's oceans does not, however, include consideration of the relative toxicities of metals. If these are included in the computation, the metals of greatest overall hazard would probably be considered as mercury, lead, zinc, cadmium and copper (see Dryssen *et al.*, 1971). It will be noted that, in general, the trace metal content of the oceans is much greater than the annual rate of metal mobilisation by man. At first sight these data suggest that the possibility of man significantly altering the oceanic content of trace metals is remote. However, the data for trace metals in the oceans include the entire marine waters of the world (volume taken as 1.37×10^{21} litres). Of this, only a small fraction may be considered to be highly productive and it is these surface—or near-surface—waters which man is preferentially polluting. Thus, all pollutants reach the marine environment via rivers or freshwater run-off or via the atmosphere; in all cases, the pollutant is introduced at, or near, the surface, where most of the active primary and secondary production occurs. If pollutants exhibit long residence times in surface waters they may accumulate in this portion of the water column and may thus affect the entire ecosphere.

By contrast to the situation described here for trace metals, where man is increasing the rate of pollutant inflow to the aquatic environment, the synthetic organochlorines would be entirely absent from these environments without the presence of man. Thus, the mere existence of organochlorines such as DDT in the aquatic ecosphere is an indictment of man's polluting nature.

Several developed countries in the northern hemisphere have banned the use of DDT for agricultural purposes (e.g. the USA, the USSR and

Sweden). This might be expected to lead to decreases in world usage of DDT. However, this is not so, due to a greatly increased usage of DDT in the tropical belt and southern hemisphere. Hence DDT has undergone a 'southward tilt' (Goldberg, 1975a). Estimates of world usage are rather uncertain, but Whittemore (1973) has suggested a current utilisation of 45–50 000 metric tons of DDT annually for agricultural purposes (Table 3)

TABLE 3

ESTIMATES OF ANNUAL UTILISATION OF DDT IN AGRICULTURAL ACTIVITIES, LATIN AMERICA, AFRICA AND ASIA. DATA ARE FOR 1973 AFTER F. W. WHITTEMORE, CITED IN GOLDBERG (1975a). TOTAL FUTURE ANNUAL REQUIREMENTS UP TO 1981 WERE ESTIMATED BY THE SAME AUTHOR AS APPROXIMATELY 69 000 METRIC TONS FOR THE SAME AREAS

Region	DDT utilisation (metric tons per year)			Total All crops
	Cotton-producing countries Cotton	Other crops	Other countries All crops	
Central America	7 580	2 550	383	10 513
South America	18 800	6 200	1 180	26 180
Africa	2 186	729	605	3 520
Asia	5 568	1 523	410	7 501
Total, all regions	34 134	11 002	2 578	47 714

and Rafatjah and Stiles (1972) predict a similar figure of 47 000 metric tons annually (between 1971 and 1981) for anti-malarial programmes. These estimates agree well with the suggested world production of DDT of 100 000 metric tons per year, about 65 per cent of this being produced by the USA (N.A.S., 1971). The integrated world production of DDT (that produced since its introduction as a pesticide) has been estimated as 2 million metric tons. Of this, 25 per cent has been transferred to the sea by run-off and via the atmosphere, according to estimates by an expert panel (N.A.S., 1971).

Because of the enormous success of DDT in controlling mosquitoes and as a pesticide for agricultural use (especially for cotton), the production of this compound has probably far outstripped that of any other organochlorine. Production estimates are, however, difficult to ascertain for any of the organochlorines (see, for example, Peakall and Lincer, 1970). Certainly DDT is generally found far more frequently (and in greater amounts) in biota than are other organochlorines although, in certain areas, such as the Baltic Sea, PCBs are found in similar amounts in seals (Helle *et al.*, 1976a, b).

As previously discussed for trace metals, the organochlorines are introduced to the marine environment at, or near, the sea surface. In the case of organochlorines, however, introduction via the atmosphere is probably by far the most important route. Calculations by Lloyd-Jones (1971) indicate that the vapour pressure of DDT is sufficient to account for the complete vaporisation of the quantity of DDT used annually worldwide. Hartley (1969) has suggested two mechanisms, termed 'wick evaporation' and 'adsorption displacement', by which DDT may be lost from soils after its application. Other authors also have emphasised the importance of the atmospheric transport of DDT (Woodwell *et al.*, 1971; Bidleman and Olney, 1974), and calculations by Galley (1974) suggested that up to 10 per cent of the annual production of DDT may be present in the atmosphere between the earth's surface and a height of 1.6 km at any one time. The most important method of removal of this compound from the atmosphere is probably via rainfall (N.A.S., 1971).

The dissipation of organochlorines via the atmosphere tends to lead to a more diffuse input of these compounds into marine waters than is evident for trace metals, which are generally introduced to the sea via rivers. However, this distinction is a matter of degree only, as both groups of pollutants are introduced via both rivers and the atmosphere to the oceans; indeed, some authors believe the atmospheric input of trace metals to be highly significant (Topping, 1974; Young and Jan, 1976, 1977). Regardless of the major entry route for organochlorines, the spraying of areas with these compounds for either agriculture or anti-malarial purposes may elicit acute localised pollution of adjacent watercourses, which may, in turn, lead to 'hot-spots' of contamination in estuarine areas. Such estuarine regions receiving run-off from agricultural catchments were considered by Butler (1966) to be the areas at greatest risk from organochlorine pollution; they may also be considered as particularly high-risk areas as regards trace metal pollution.

C. THE PARTITIONING OF TRACE METALS AND ORGANOCHLORINES IN NATURAL WATERS

The above discussion has shown that man is mobilising or synthesising appreciable quantities of trace metals and organochlorines. These compounds (or a significant proportion of them) must eventually reach the aquatic environment, which may be envisaged as a final sink for most pollutants. The effects elicited by such contamination of rivers or marine

TABLE 4

CONCENTRATIONS OF METALS IN SATURATED SOLUTION IN AERATED SEAWATER OF pH 7.8-8.2 AND TEMPERATURE 18-23°C (KRAUSKOPF, 1956) AND THEIR COMPARISON WITH PUBLISHED DATA FOR THE ACTUAL CONCENTRATIONS OF METALS FOUND IN SEAWATER. (FROM THE REVIEW OF PYTKOWICZ AND KESTER (1971).)

Metal	Compound added	Concentration in saturated solution (mg/litre)		Concentration in seawater ($\mu\text{g/litre}$)
		Minimum	Maximum	
Ag	AgNO ₃	2.2	2.5	0.04-1.50
Cd	CdCl ₂	4.0	1 000	0.02-0.25
Co	CoCl ₂	30	200	0.005-4.10
Cr	K ₂ CrO ₄		'very high'	0.04-0.43
Cu	CuSO ₄	0.6	0.8	0.20-27.0
Hg	HgSO ₄	↓18	700	0.03
Fe	FeCl ₃		0.005 ^a	0.03-62.0
Mo	(NH ₄) ₂ MoO ₄	25	750	0.24-12.2
Ni	NiCl ₂	23	455	0.13-43.0
Pb	Pb(NO ₃) ₂	0.3	0.7	0.02-0.40
V	VOSO ₄	4.0	150	2.0-3.0
W	Na ₂ WO ₄	2.0	280	0.10
Zn	ZnCl ₂	1.2	2.5	1.0-50.0

^a Fukai and Huynh-Ngoc (1968).

waters depend on several factors, but the most important of these factors is dosage. It is thus vital for man to be able to quantitate the abundance of trace metals and organochlorines in aquatic ecosystems.

Krauskopf (1956) concluded from his studies of the solubilities of trace metals in seawater that, under normal conditions, aerated seawater in open oceans is very considerably undersaturated with trace elements. The minimum concentrations attainable in solution thus varied from 0.3 mg/litre for lead to 118 mg/litre for mercury (Table 4). As the actual levels of elements in solution in seawater (even in the more highly contaminated coastal waters) are in the $\mu\text{g/litre}$ range (Table 4), the above conclusion is clearly upheld. Most trace metals will thus rarely, if ever, exceed their solubilities in seawater, and all the metal could be maintained in solution under normal conditions. The only exception of any real importance is iron, which exhibits very low solubility in seawater and is maintained in the water column almost entirely by adsorption to suspended particulates.

Studies of trace metals in seawater, however, have shown that no metal exists entirely in solution. That which is in solution is in the form of simple

or complex ions. In addition, some metal is associated with inorganic or organic particulates of varying size and composition. Lastly, a certain percentage of the total metal present exists as chelates or colloids; these compounds are difficult to assign to either soluble or particulate phases and are generally poorly understood. The percentage of the total metal in each of these phases varies not only with the water body (e.g. significant differences exist in metal partitioning between the phases in fresh water and in salt water), but also with the particular metal considered. For example, in marine waters, iron is present almost completely in association with inorganic or organic particulates (Head, 1971; Preston *et al.*, 1972), whereas cadmium favours the soluble fraction to a great extent (Preston *et al.*, 1972), but may also associate with microplankton (Bruland *et al.*, 1978). The tendency of each metal to form chelates also varies widely; for example, copper is probably the only element to exhibit significant chelate formation with humic materials in salt waters whereas both copper and mercury are thought to form chelates with humic substances in fresh waters (Mantoura *et al.*, 1978). The effects of chelation of metals on their toxicity and biological availability are certainly more pronounced in fresh waters than in marine areas, and this factor may, in certain cases, be paramount in determining species viability in the former ecosystems.

It is interesting to compare the probable partitioning of organochlorines between the soluble and particulate fractions of either freshwater or seawater with that of trace metals. Organochlorines exhibit low solubilities in water (Table 5), although it should be noted that authors rarely agree on the absolute solubilities of any one of these compounds, as considerable differences are found with differences in research methodologies and with particle size and temperature (Gunther *et al.*, 1968).

This low solubility of organochlorines in water must be seen in perspective. It is clear that if concentrations of any organochlorine exceed the solubility of that compound in a water body, the excess must be present in a phase other than the solution phase; in reality, the excess would be associated with organic and inorganic particulate material by surface adsorption. However, although the solubility of these compounds in water is low, their usual concentrations are still lower. Thus, the lowest estimate of the solubility of DDT in water is $1.2 \mu\text{g/litre}$ (Bowman *et al.*, 1960). Reports of the Southern California Coastal Water Research Project indicate that even at the extremely highly polluted Los Angeles sewage outfall, average DDT concentrations ranged from $7.5 \mu\text{g/litre}$ in 1973 to $2.6 \mu\text{g/litre}$ in 1976. Other Californian municipal wastewaters generally contained much less DDT than did the Los Angeles outfall. Even the Los Angeles outfall