NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL de RECHERCHE sur les EAUX

INFLUENCE OF TROPHIC STATUS ON THE BEHAVIOUR OF CONTAMINANTS IN AQUATIC SYSTEMS

R.M. Baxter, J.H. Carey, D.R.S. Lean and B.K. Burnison

NWRI Contribution No. 90-26

MANAGEMENT PERSPECTIVE

In order to assess the likely persistence of environmental contaminants in natural waters it is necessary to take into account the interaction between these contaminants and the natural chemical compounds and living organisms present in water bodies. These in turn depend on the trophic status of the water, i.e. the degree of eutrophy (presence of algal nutrients leading to primary productivity) and dystrophy (presence of humic matter).

The available information regarding these interactions is reviewed, and their possible practical significance is discussed. It appears that microbial oxidation of contaminants of low persistence may be slightly enhanced both in eutrophic and oligotrophic lakes, and reductive degradation even of relatively persistent contaminants may be enhanced in eutrophic lakes, in comparison with oligotrophic clearwater lakes. Naturally occurring coloured material in dystrophic lakes and perhaps also in eutrophic lakes may facilitate the photochemical destruction of some contaminants. Binding of hydrophobic contaminants by living organisms in eutrophic lakes, and by dissolved or particulate organic matter in both types of lakes, may hamper their uptake by fish, and eventually contribute to their immobilization in sediments.

All these processes may serve in some degree to mitigate the impacts of environmental contamination with synthetic organic chemicals.

PERSPECTIVE DE GESTION

Pour évaluer les probabilités de persistance d'agents de contamination environnementale dans les eaux naturelles, il faut tenir compte de l'interaction de ces agents de contamination avec les composés chimiques naturels et les organismes vivants présents dans les plans d'eau. Ceux-ci dépendent quant à eux de l'état trophique de l'eau, c.-à-d. du degré d'eutrophie (présence d'éléments nutritifs fournis par les algues, conduisant à une productivité primaire), et de dystrophie (présence de matières humiques).

On examine l'information disponible sur cette interaction et l'on discute ses répercussions pratiques possibles. Il semble que l'oxydation microbienne des agents de contamination à faible persistance puisse augmenter légèrement tant dans les lacs eutrophes que dans les lacs oligotrophes et que la dégradation réductive, même d'agents de contamination relativement persistants, puisse être plus importante dans les lacs eutrophes que dans les lacs oligotrophes d'eau limpide. Les substances colorées se trouvant à l'état naturel dans les lacs dystrophes et peut-être aussi dans les lacs eutrophes peuvent faciliter la destruction photochimique de certains agents de contamination. La

fixation d'agents de contamination hydrophobes par les organismes vivants dans les lacs eutrophes et par des matières organiques dissoutes ou sous forme de particules dans les deux types de lacs peut entraver l'absorption de ces agents par les poissons et, par la suite, contribuer à leur immobilisation dans les sédiments.

Tous ces processus peuvent servir dans une certaine mesure à corriger l'impact de la contamination environnementale par les produits chimiques organiques de synthèse.

RÉSUMÉ

Baxter, R.M., Carey, J.H., Lean, D.R.S. et Burnison, B.K. 1990. Influence de l'état trophique sur le comportement des agents de contamination dans les systèmes aquatiques

Le problème de l'eutrophisation par l'enrichissement en matières nutritives et la contamination par des agents de contamination persistants ont toujours été considérés par les chercheurs et les gestionnaires des ressources hydriques comme des phénomènes sans rapport l'un avec l'autre. Or, on dispose aujourd'hui d'indications récentes selon lesquelles le devenir des agents de contamination organiques dans l'écosystème aquatique serait fonction de l'état trophique du système. On a également des indications voulant que la matière organique dissoute dans les eaux dystrophes ou humiques agisse sur la dynamique des agents de contamination. Les mécanismes qui peuvent être en cause sont notamment les changements qui surviennent dans les capacités métaboliques des organismes en fonction de la modification de l'état trophique, la dégradation réductive dans l'hypolimnion anoxique des eaux très productives, la fixation des agents de contamination par les organismes ou les matières organiques dissoutes, et la dégradation photochimique induite par les

molécules absorbant la lumière. On discute les répercussions possibles de ces processus.

ABSTRACT

Baxter, R.M., Carey, J.H., Lean, D.R.S. and Burnison, B.K.1990. Influence of trophic status on the behaviour of contaminants in aquatic systems.

The problems of eutrophication through nutrient enrichment and contamination with persistent contaminants have traditionally been regarded as unrelated by water scientists and managers, but recently evidence has appeared suggesting that the fate of organic contaminants in an aquatic ecosystem is influenced by the trophic state of the system. There is also evidence that the dissolved organic matter in dystrophic, or humic,waters may influence contaminant dynamics. Mechanisms that may be involved include changes in the metabolic capabilities of organisms with changes in trophic state; reductive degradation in the anoxic hypolimnia of highly productive waters; binding of contaminants by dissolved organic matter or organisms, or photochemical degradation induced by light-absorbing molecules. The possible significance of these processes is discussed.

INTRODUCTION

The trophic status of most natural waters can be defined in terms of eutrophy and dystrophy. The degree of eutrophy is determined primarily by the input of inorganic nutrients, but may be modified by other factors such as depth of mixing of the water and the nature of the biological community. Thus apparent eutrophy may be increased by the presence of planktivorous fish, which prey on zooplankters that would otherwise feed on algae (Mazumder et al. 1990). Eutrophic waters are green and of low transparency because of the presence of large populations of phytoplankton. There is also sometimes increased growth of attached algae or macrophytes. Primary productivity is high, leading to relatively high concentrations in the water of dissolved organic material (DOM) excreted by the primary producers or released by them as they become senescent and die (Cole 1982; Chrost & Faust 1983). This organic matter supports a

population of heterotrophic bacteria (Bird & Kalff 1984; Cole et al. 1988; Rippey & Cabelli 1989), and the settling of organic material towards the bottom permits heterotrophic oxidative activity in the sediments and hypolimnion, leading to depletion of oxygen. In extreme cases the hypolimnion may become completely anoxic. Natural lakes of a very wide range of eutrophy exist,from very clear ultraoligotrophic lakes such as Lake Tahoe in which the Secchi depth may be 40 m or more (Goldman 1981), to extremely productive hypereutrophic lakes like certain African crater lakes in which the Secchi depth is measured in centimeters and which may attain levels of primary productivity approaching the theoretically possible upper limit (Talling et al. 1973).

Dystrophic waters are of low transparency and reddish-brown in colour because of the presence of relatively stable coloured organic acids, the so-called humic substances. In spite of two centuries of research (Stevenson 1982) the structures of these substances are still only imperfectly known. They are produced by the extensive modification of compounds of biochemical origin and appear to be of moderate to high molecular weight and of mixed aromatic and aliphatic structure. For the present discussion, their most important properties are that they are coloured and amphiphilic, that is they contain both hydrophilic and hydrophobic functional groups. Most of the dissolved humic material in natural waters is leached from the soil of the drainage basin (Rasmussen et al. 1989), but some may be produced in lakes or bogs by the decomposition of plant material. Such waters are characterised by low pH and high DOM. The total biomass and primary productivity are generally considered to be low,as the term "dystrophic" ("ill-nourished") implies. This may be true of the pelagial region, but the littoral zone often supports a highly productive community of macrophytes (Wetzel 1983). Although most of the dissolved organic matter is resistant to attack by microorganisms, enough is sometimes degradable to support a moderate bacterial population and contribute a significant heterotrophic component to the food web. Dystrophic lakes are commonly found in forested areas, particularly on granitic rocks as in the northern part of Fenno-Scandinavia, or the Laurentian Shield of northern North America.

In the well-watered regions of much of North America and western Europe most waters are naturally oligotrophic. About a century ago some lakes in these parts of the world began to show signs of increasing eutrophication. It is often said that eutrophication represents a natural process in the evolution of lakes. This is probably true under most conditions, although there is a tendency towards oligotrophication as well (Margalef 1968). However the changes that were observed were much too rapid to represent a natural aging process and were clearly due to the enrichment of the waters by domestic drainage (Hasler 1947). This phenomenon, known as cultural eutrophication, was observed

more and more frequently over the years as populations and associated agricultural and industrial activities increased throughout the world generally and within the drainage basins of lakes in particular, and became particularly evident in the 1950s and 1960s. This trend caused increasing concern in the minds of limnologists and freshwater biologists, as well as the general public. The increased algal populations of many lakes were found esthetically unpleasing, and the lowered oxygen concentrations were deleterious to fish populations, which were reduced or replaced by less desirable species.

A well known example is that of Lake Washington (State of Washington, U.S.A.). Available data beginning in 1933 showed evidence of increasing eutrophication, which was attributed to the influx of nutrient-rich secondary sewage effluent (Edmondson et al. 1956). Decreasing the amount of effluent entering the lake, and eventually stopping it completely, allowed processes tending toward oligotrophication to become dominant, and by 1975 the lake was considered to have recovered (Edmondson & Lehman 1981). Another region which gave cause for concern at this time was the Laurentian Great Lakes where signs of eutrophication were apparent by the mid 1960s (Beeton 1965). The situation seemed particularly alarming in Lake Erie, the shallowest of the lakes. Not only were extensive growths of algae,both attached and planktonic species, observed in many parts of the lake,but large parts of the hypolimnion were found to be anoxic during periods of stratification. After some controversy it was generally agreed that phosphorus was the limiting nutrient in the eutrophication of these lakes and an international agreement was reached between Canada and the United States to control the influx of this element. Here again the eutrophication process was arrested and to some degree reversed (Barica 1989), although late-summer deoxygenation of the hypolimnion continues (Boyce et al. 1987).

The limnological mechanisms involved in eutrophication and the measures to be taken for its control are now believed to be fairly well understood (Vollenweider 1969,1975). There are still many areas in the world where eutrophication continues to be a problem, but public concern has generally declined over the past decade (Allan 1989).

Cultural dystrophication appears to be much less common than cultural eutrophication, but it may occur under certain circumstances. One instance of this was observed at Southern Indian Lake in the northern part of the Canadian province of Manitoba. Here construction of a hydroelectric facility raised the water level of the lake by about three meters, flooding a substantial area where permafrost was overlaid by moss and peat. Humic material leaching into the water significantly depressed the primary productivity of the lake (Guildford et al. 1987).

As public concern about cultural eutrophication has

declined, concern about all aspects of the contamination of the environment by potentially noxious substances has increased, and shows no sign of waning (Allan 1989). A number of organic halides, and especially organic chlorides, have received the greatest attention. Organic compounds containing halogen atoms are by no means unknown in nature. Hundreds of compounds containing chlorine, bromine,and iodine and a few containing fluorine are produced by living organisms (Faulkner 1980; Engvild 1986; Neidleman & Geigert 1986). These substances probably play significant roles in the physiology and ecology of the organisms that produce them,but in general they are either chemically unstable or susceptible to attack by naturally-occurring microorganisms (Larsson & Lemkemeier 1989; King 1988) and consequently do not accumulate in the environment. A few may conceivably have some environmental impact because they are produced in large quantities and are moderately persistent (Cook et al. 1988). The most important of these is perhaps methyl chloride, which is listed as a priority pollutant by the U.S. EPA (Keith & Telliard 1979) and is produced by many species of terrestrial fungi (Hutchinson 1971; White 1982; Harper 1985; Harper et al. 1988). The input of this compound to the environment from natural processes far exceeds that from human activities (Harper et al. 1988). It is widely distributed in the atmosphere (Lovelock 1975; Rasmussen et al. 1980; Singh et al. 1983) and gives cause for concern because it may contribute to the destruction of stratospheric ozone.

The accumulation of methyl chloride is limited however by its susceptibility to eventual destruction by chemical (Lovelock 1975) and biochemical (Hartmans et al. 1986) processes. The behaviour of many synthetic organochlorine compounds is quite different. Many of these are exceedingly resistant to chemical degradation under the conditions prevailing in the environment, and also to biochemical degradation. Indeed persistence in the environment was originally considered a desirable characteristic in compounds used as pesticides.

Microbiologists have well-established techniques for obtaining cultures of microorganisms capable of oxidizing compounds of interest and using the carbon and energy derived from this process to sustain growth. These techniques were so successful with a variety of compounds that it was once widely believed that it would be possible to obtain a culture capable of oxidizing any organic compound whatsoever. This now seems extremely doubtful, and some synthetic compounds appear to be totally recalcitrant (Alexander 1981), probably because they are so different in structure from any compounds found in nature that no organisms have evolved the ability to produce enzymes to attack them. Other compounds may undergo some degree of oxidative modification in the presence of organisms growing on other substrates, a process sometimes referred to as co-metabolism (Horvath 1972) although this term has been criticized (Hulbert &

Krawiec 1977). Still others may be oxidized at the concentrations commonly used in the laboratory, but not at the much lower concentrations occurring in nature (Boethling & Alexander 1979).

More recent studies have shown that for certain substances reductive processes are much more effective than oxidative ones in bringing about transformations or degradation (Macalady et al.1986). Many halogenated compounds in particular seem to be susceptible to partial or complete degradation by reductive dehalogenation (Kuhn & Suflita 1989). Several types of reaction appear to be involved. One type, which is effective against many alkyl halides, is reduction by reduced iron porphyrins and perhaps other metal-containing compounds. For example DDT [1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane] is readily converted to DDD [2,2-Bis(4-chlorophenyl)-1,1-dichloroethane] (Zoro et al. 1974) which may be further dechlorinated (Quirke et al. 1979). This process does not appear to be enzymatic. Other non-enzymatic processes may involve reduction by iron minerals or humic substances (Curtis & Reinhard 1989) or reductants that are not yet identified (Wolfe 1990). Another process which is effective against aryl halides seems to be closely associated with microbial methanogenesis, and is most probably enzymatic (Kuhn & Suflita 1989).

The first organochlorine compound to be used on a large scale as a pesticide was DDT. This substance saved millions of human lives and at first seemed almost totally harmless to human beings even when used in very large quantities in an almost reckless manner (Metcalf 1973; Spindler 1983). It was perhaps its apparent innocuousness that led to the subsequent equally careless use of a variety of other organochlorine pesticides, many of which are less benign. Throughout the 1940s and 1950s the use of these steadily increased. At the same time more and more incidents of deleterious effects were observed and reported. These were described with great literary skill in 1962 by Rachel Carson in "Silent Spring", one of the most influential books of our time. Since then the problem of environmental contaminants has given rise to increasing public concern, and more and more research to determine the extent and seriousness of the problem. DDT and its transformation products DDE [2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene] and DDD were found to be virtually ubiquitous in organisms throughout the world. A number of other pesticides were found to be almost equally widely distributed in sediments and sometimes in organisms.

It is not only substances that are deliberately released into the environment that may accumulate there. In 1966 Jensen, looking for DDT and its products in fish and birds in Sweden, found additional organochlorine compounds which proved to be chlorinated biphenyls (Jensen 1972). A little later ten Noever De Brauw and his colleagues (1973), examining seals for

organochlorine compounds, and Kaiser (1974, 1978), looking for chlorinated biphenyls in fish from Lake Ontario, found yet another compound which proved to be mirex (dodecachloro-octahydro-1,3,4-metheno-2H-cyclobuta[c,d]pentelene). Chlorinated biphenyls were not pesticides, but were used industrially in the form of complex mixtures referred to as polychlorinated biphenyls (PCBs). Mirex had been used as a pesticide in some parts of the world, but probably not in the Great Lakes basin. It was manufactured there but probably only used for industrial purposes. It was clear from these observations that serious environmental contamination could result from accidental spillage or release from dumps.

Even compounds that have no industrial uses, and have never been deliberately produced in any quantity, may accumulate. These include various chlorinated styrenes such as octachlorostyrene, which have been found in organisms and sediments in various parts of the world (ten Noever De Brauw & Koeman 1972/73; Kaminsky & Hites 1984). These are apparently produced by the reaction of chlorine with the binders in graphite electrodes used in chlorine-alkali plants (Kaminsky & Hites 1984).

There is evidence that both dystrophy and eutrophy may influence the behaviour of contaminants in ways that are desirable from the human point of view. The evidence regarding dystrophy mostly comes from laboratory experiments with humic substances which have clearly established that various interactions between these substances and contaminants can occur (Suffet & MacCarthy 1989), although the extent and importance of these interactions in nature is still uncertain.

The evidence regarding eutrophy is derived largely from field observations. Bird & Rapport (1986) compiled a large body of data on the concentrations of several contaminants in a number of organisms in the Laurentian Great Lakes, and concentrations were consistently higher in Lake Ontario organisms than in those from the more eutrophic Lake Erie. For some contaminants this could be explained by contamination of Lake Ontario from sources below Lake Erie. For others however, such as PCBs, loadings for the two lakes appear not to differ significantly (International Joint Commission 1987). Observations like these suggest that the problem of eutrophication may be interrelated with the problem of contamination , so that neither of these can be considered in isolation (Allan 1989). The general idea is that eutrophication serves in some way to buffer the effects of contamination.

Because of the potential significance of this for water managers as well as its scientific interest, the Lakes Research Branch of the National Water Research Institute in Burlington, Ontario has undertaken a Nutrient-Contaminants Interactions Project to investigate this matter further. To simplify the study we have chosen to investigate a group of small Ontario lakes

lying on both sides of the southern edge of the Canadian Shield. Lying as they do in an area of transition between sedimentary and igneous bedrock they display a considerable range in the chemical composition of their waters. There is virtually no industry in the vicinity of these lakes.

In an initial study (Carey et al. 1989), zooplankton samples from more than 30 of these lakes were analyzed for several persistent contaminants. To assess the trophic status of the waters, springtime total phosphorus concentrations were also measured. The relative proportions of the various compounds proved to be very similar in all samples, indicating that all the lakes were receiving them from the same source, presumably the atmosphere. However when the concentrations of several contaminants in zooplankton were plotted against springtime total phosphate concentrations of the waters, a strong inverse correlation was found.

It is possible that the lower contaminant concentrations observed in samples from more eutrophic lakes are not entirely due to an effect of eutrophy on contaminant dynamics, but that both are due to the same cause. For example, relatively shallow lakes tend to be more productive than deeper ones. They also tend to have shorter flushing times, so that contaminants may be washed away more quickly. Lake Erie is considerably shallower than Lake Ontario. It seems unlikely however that this is the whole story, and several mechanisms whereby the trophic state of a water body may influence the fate of contaminants within it are discussed below.

TROPHIC STATE AND MICROBIAL OXIDATION

There is some evidence that in highly dystrophic lakes bacterial populations have developed which are able to degrade the natural aromatic compounds that are part of the humic material in the lake water, and are also capable of degrading moderately persistent synthetic compounds such as chlorophenols. Such organisms were less abundant in clear-water lakes (Larsson & Lemkemeier 1989; Larsson et al. 1988). There seems to be no reason to suppose however that eutrophic conditions would favour the growth of such organisms. Algae can oxidize certain contaminants such as alkyltin and alkyllead compounds (Maguire et al. 1984; Wong et al. 1987; Lee et al. 1989) and it is conceivable that the populations of mixed heterotrophic organisms supported by the dissolved organic matter in eutrophic lakes might be capable of cometabolizing certain contaminants. There is no experimental evidence bearing on this question for the Great Lakes. Microbial oxidation is probably of little or no significance for the contaminant dynamics of our small study lakes, since the relative proportions of the various contaminants are fairly constant throughout the lakes, and it seems unlikely

that all would be degraded at the same rate.

Humic material can enhance the biodegradation of certain contaminants under laboratory conditions; the mechanism of this is unclear (Liu et al. 1983). It is not known if any of the dissolved organic compounds in eutrophic lakes can behave in this way.

On the basis of available evidence it seems unlikely that either eutrophy or distrophy is likely to have much effect on the oxidative degradation of highly persistent contaminants such as chlorinated pesticides and PCBs.

TROPHIC STATE AND REDUCTION

There is some evidence that eutrophy may favour the reduction of some contaminants in the Great Lakes. DeVault et al. (1988) measured the concentrations of several contaminants in fall run Coho Salmon in the five lakes. Their results for DDT and its transformation products, DDE and DDD, are interesting. Average total concentrations for samples from a number of stations in each lake ranged from 0.03 ug/g in Lake Superior and 0.06 ug/g in Lake Erie to 0.47 ug/g in Lake Ontario. DDE was the predominant compound in all the lakes, ranging from 70% in Lake Erie to 90% in Lake Michigan. However DDD made up 18% of the total in Lake Erie,compared with 8% in Lake Ontario and 2 - 4% in the other lakes. This strongly suggests that the anoxic hypolimnion of Lake Erie provided a milieu more favourable to reduction than was found in the other lakes. In our study lakes as well, the proportion of DDD appeared to be highest in the most eutrophic of the lakes, although no relationship between the proportion of DDD and the degree of eutrophy was evident in the other lakes (Carey et al. 1989).

Humic substances may act as reductants for certain easily-reduced contaminants (Curtis & Reinhard 1989) but there is no evidence that they have any effect on more persistent substances.

TROPHIC STATE AND INDIRECT PHOTODEGRADATION

Indirect photodegradation is a process in which light is absorbed by one molecule (the initiator) which thereby becomes excited and reacts with another molecule which then undergoes degradation. This is in contrast to direct photodegradation in which the reactant absorbs light directly. The possible significance of indirect photodegradation in the destruction of environmental contaminants was first revealed by Ross and Crosby (1973) who observed that ethylenethiourea was degraded in boiled agricultural drainage waters in the light but not in the dark. Later Zepp et al.(1976) found that photolysis of the insecticide methoxychlor proceeds much more rapidly in natural

water samples than in distilled water.

Subsequent work has shown that the humic substances found in dystrophic lakes, as well as the coloured material in the sea, can act as effective initiators for a variety of photochemical reactions. These studies have recently been reviewed (Cooper et al 1989; Hoigne et al.1989; Zepp 1988). An excited humic molecule may react with another molecule, for example an enviromental contaminant,and modify it or combine with it, or it may react with a molecule of oxygen to produce highly reactive species such as singlet oxygen or the superoxide radical ion, which may in turn dismutate to the more stable hydrogen peroxide. Other reactive species, such as hydrated electrons and organoperoxy radicals,may also be formed. The precise role of these highly reactive species in the transformation of environmental pollutants can not yet be defined,but there seems little doubt that it is an important one.

The photochemical behaviour of the much less modified bioorganic material found in eutrophic lakes has been less studied. Aromatic compounds such as the amino acid tryptophan can take part in photochemical reactions producing hydrogen peroxide (Draper & Crosby 1983a) or the superoxide radical anion (Draper & Crosby 1983b). Once formed,hydrogen peroxide can take part in further photochemical reactions,including the photooxidation of a number of pesticides (Draper & Crosby 1984). Tryptophan,even at the low concentrations at which it may exist in natural waters, was found to act as an initiator for the photolysis of hexachlorobenzene, and protein extracted from a pond water was also active (Hirsch & Hutzinger 1989). The photochemical conversion of mirex to photomirex (8-monohydro mirex) was found to be more rapid in water from Lake Ontario than in distilled water (Mudambi & Hassett 1988). The action spectrum for the reaction in lake water was different from that in the presence of humic material.

BINDING OF CONTAMINANTS BY ORGANIC MATTER

Hydrophobic contaminants such as chlorinated hydrocarbons can be bound by organic material in soils and sediments (Karickhoff 1981; Caron & Suffet 1989) and by both particulate and dissolved organic material in water (Kile & Chiou 1989; Henry et al. 1989; Senesi & Chen 1989). Binding to particulate or sedimentary organic matter tends to remove contaminants from the water column whereas binding to dissolved organic matter tends to maintain them in solution, but both diminish their uptake by organisms. The extent of the binding of contaminants to dissolved humic material in natural waters has been overestimated in the past because of the use in binding experiments of commercial humic acid preparations, which bind lipophilic molecules much more strongly than do naturally-occurring aquatic humic substances

(Chiou et al. 1987). Nevertheless the effect is a significant one. The dissolved organic material in non-humic lakes, whatever their degree of eutrophy,probably represents a mixture of almost all types of biochemicals (Margalef 1983) of all degrees of hydrophobicity and hydrophilicity. It might be expected that these would differ accordingly in their ability to interact with contaminants, and perhaps in general to be less effective than humic substances. This seems to be borne out by a study on the sorption of polynuclear hydrocarbons by dissolved organic matter from Lake Michigan, which proved to be much less effective than DOM from a humic lake (Morehead et al 1986). On the other hand water from the Niagara River was found to contain a component that bound lipophilic contaminants so strongly that they could not be extracted by the procedures most commonly used (Maguire & Tkacz 1989). This water would not be expected to contain a great deal of humic material because it is largely derived from Lake Erie,where the concentration of humic material is low (D.R.S.Lean, unpublished).

Our group has undertaken a study of the properties of DOM from the lakes of our study sites and elsewhere. The DOM in water samples is fractionated according to molecular weight using a series of four filters in a tangential flow apparatus. Substantial quantities of several size fractions have been isolated, and their chemical characteristics and interaction with contaminants are being examined. A considerable part, especially of the higher molecular weight fractions, proved to be carbohydrate (Burnison & Leppard 1990). Much of this consists of acidic polysaccharides probably derived from the mucilagenous sheathes of blue-green algae (Burnison 1978) and exists in the form of small fibrils (Burnison & Leppard 1983, 1984). These can probably bind cations (Leppard et al. 1977), but because of their hydrophilic character their capacity to bind hydrophobic organic contaminants is uncertain.

BINDING OF CONTAMINANTS BY BIOMASS

This may explain the results from our group of small lakes. It has recently been shown (Yan 1986) that in a group of lakes probably not unlike ours, total phosphate concentration was a reasonably good predictor of zooplankton biomass. Hence the inverse correlation observed between total phosphate and contaminant concentration may well have represented a similar relationship between concentration and biomass. The results reported for the Great Lakes probably cannot be explained so simply. The differences reported between Lake Ontario and Lake Erie were much bigger, and were observed at a higher trophic level than in the smaller lakes. Species differences between the biota of the two lakes may play a role. The uptake of PCBs (and probably of other persistent hydrophobic contaminants) by microorganisms is believed to be controlled largely by sorption

to surfaces, and in larger organisms by partitioning into lipid phases (Falkner & Simonis 1982). Difference in size, and hence of the surface/volume ratio,of the planktonic algae, species and seasonal differences in nature and amount of lipids in larger organisms (Wainmann & Lean In press), and differences in feeding preferences at all trophic levels, might be expected to be considerably more significant than simple dilution.

CONCLUSIONS

The heterotrophic bacterial populations of both eutrophic and dystrophic lakes may have some capacity to oxidize moderately persistent contaminants. The organisms in dystrophic lakes may be somewhat more effective against substances like chlorophenols because the partially aromatic character of the naturally-occurring humic substances may provide a selective medium for the growth of organisms able to attack aryl groups. Certain species of algae which may occur in eutrophic lakes may also be able to attack some contaminants. It seems unlikely however that any of these organisms are effective against the most persistent contaminants such as chlorinated pesticides and PCBs.

Reductive processes seem likely to be more significant than oxidative ones in destroying contaminants in the environment. In lakes that are eutrophic enough to develop anoxic hypolimnia, reductive degradation of a variety of contaminants may occur. Even persistent contaminants such as chlorinated pesticides may be attacked. Dystrophic lakes probably provide less favourable conditions than do eutrophic lakes for these processes, although reductive degradation of moderately persistent contaminants may occur.

There is some evidence that compounds which are likely to be present in eutrophic waters, such as aromatic amino acids and proteins containing them , may act as initiators for the photochemical degradation of contaminants. There is considerably more evidence that the coloured compounds in humic waters may act in this way.

Eutrophic lakes may accumulate considerable quantities of organic compounds. Whether these are of a kind that will be effective in binding hydrophobic contaminants seems uncertain at this time. On the other hand there seems to be little doubt that the amphiphilic compounds in dystrophic water can bind hydrophobic substances strongly enough to have a profound effect on their dynamics in aquatic ecosystems.

Finally, the higher populations of organisms at several trophic levels that are likely to be present in eutrophic waters must almost certainly serve to dilute the concentrations of contaminants in the total biomass. This is not likely to be very

significant in the smaller populations usually found in dystrophic lakes.

REFERENCES

Alexander, M. 1981. Biodegradation of chemicals of environmental concern. Science 211: 132 - 138.

Allan, R.J. 1989. Anthropogenic organic chemical pollution of lakes with emphasis on the Laurentian Great Lakes. In: J. Salanki & S. Herodek (Editors), Conservation and Management of Lakes. Symp. Biol. Hung. 38: 217 - 243.

Barica, J. 1989. Recovery of the Laurentian Great Lakes, 1970-1985: eutrophication aspects. In: J. Salanki & S. Herodek (Editors), Conservation and Management of Lakes. Symp. Biol. Hung. 38: 43 - 59.

Beeton, A.M. 1965. Eutrophication of the St.Lawrence Great Lakes. Limnol. Oceanogr. 10: 240 - 254.

Bird, D.F. & Kalff, J. 1984. Empirical relationships between bacterial abundance and chlorophyll concentration in fresh and marine waters. Can. J. Fish. Aquat. Sci. 41: 1015 - 1023.

Bird, P.M. & Rapport, D.J. 1986. State of the Environment Report for Canada. Environment Canada, Ottawa. 263 pp.

Boethling, R.S. & Alexander, M. 1979. Effect of concentration of organic chemicals on their biodegradation by natural microbial communities. Appl. Environ. Microbiol. 37: 1211 - 1216.

Boyce, F.M., Charlton, M.N., Rathke, D., Mortimer, C.H. & Bennett, J. 1987. Lake Erie research: recent developments, remaining gaps. J.Great Lakes Res. 13: 826 - 840.

Burnison, B.K. 1978. High molecular weight polysaccharides isolated from lake water. Verh. Internat. Verein. Limnol. 20: 353 - 355.

Burnison, B.K. & Leppard, G.G. 1983. Isolation of colloidal fibrils from lake water by physical separation techniques. Can. J. Fish. Aquat. Sci. 40: 373 - 381.

Burnison, B.K. & Leppard, G.G.1984. Ethanol fractionation of lacustrine colloidal fibrils. Can.J. Fish. Aquat. Sci. 41: 385 - 388.

Burnison, B.K. & Leppard, G.G. 1990. Isolation of DOC from lakes

by ultrafiltration. (Abstract). Abstracts of papers for the 1990 Annual Meeting, ASLO, Williamsburg, Virginia.

Carey, J.H., Lean, D.R.S., Taylor, W.D. & McQueen, D.J. 1989. The influence of lake trophic status on concentrations of atmospherically-transported organochlorine contaminants in lake zooplankton. NWRI Contribution No. 89-28.

Caron, G. & Suffet, I.H. 1989. Binding of nonpolar pollutants to dissolved organic carbon. In: I.H.Suffet & P. MacCarthy (Editors), Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C., pp. 118 - 130.

Chiou, C.T., Kile, D.E., Brinton, T.I., Malcolm, R.L., Leenheer, J.A. & MacCarthy, P. 1987. A comparison of water solubility enhancements of organic solutes by aquatic humic materials and commercial humic acids. Environ. Sci. Technol. 21, 1231 - 1234.

Chrost, R.H. & Faust, M.A. 1983. Organic carbon release by phytoplankton: its composition and utilization by bacterioplankton. J. Plankton Res. 5: 477 - 493.

Cole, J.J. 1982. Interactions between bacteria and algae in aquatic systems. Ann. Rev. Ecol. Syst. 13: 291 - 314.

Cole, J.J.,Findlay, S. & Pace, M.L. 1988. Bacterial production in fresh and saltwater ecosystems: a cross-system review. Mar. Ecol. Prog. Ser. 43: 1 - 10.

Cook, A.M. Schotz, R. & Leisinger, Th. 1988. Mikrobieller Abbau von halogenierten aliphatischen Verbindungen. Wasser Abwasser 129: 61 - 69.

Cooper, W.J.,Zika, R.G., Petasne, R.G.& Fisher, A.M. 1989. Sunlight-induced photochemistry of humic substances in natural waters: major reactive species. In: I.H. Suffet & P. MacCarthy (Editors). Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C., pp. 333 - 362.

Curtis, G.P. & Reinhard, M. 1989. Reductive dehalogenation of hexachlorohexane by aquifer material. (Abstract). Preprints of papers presented at the 197th ACS National Meeting, Dallas TX, April 9 - 14, 1989. Vol. 29, No. 1. pp. 85 - 86.

DeVault, D.S., Clark, J.M., Lahvis, G. & Weishaar, J. 1988. Contaminants and trends in fall run Coho Salmon. J. Great Lakes Research 14: 23 - 33.

Draper, W.M. & Crosby, D.G. 1983a. The photochemical generation of hydrogen peroxide in natural waters. Arch. Environ. Contam.

Toxicol. 12: 121 - 126.

Draper, W.M. & Crosby, D.G. 1983b. Photochemical generation of superoxide radical anion in water. J. Agric. Food Chem. 31: 734-737.

Draper, W.M. & Crosby, D.G. 1984. Solar photooxidation of pesticides in dilute hydrogen peroxide. J. Agric. Food Chem. 32: 231 - 237.

Edmondson, W.T.,Anderson, G.C. & Peterson, D.R. 1956. Artificial eutrophication of Lake Washington. Limnol. Oceanogr. 1: 47 - 53.

Edmondson, W.T. & Lehman, J.T. 1981. The effect of changes in the nutrient income on the condition of Lake Washington. Limnol. Oceanogr. 26: 1 - 29.

Engvild, K.C. 1986. Chlorine-containing natural compounds in higher plants. Phytochem. 25: 781 - 791.

Falkner, R. & Simonis, W. 1982. Polychlorierte Biphenyle (PCB) im Lebensraum Wasser (Aufnahme und Anreicherung durch Organismen-Probleme der Weitergabe in der Nahrungspyramide). Arch. Hydrobiol. Beih. Ergebn. Limnol. 17: 1 - 74.

Faulkner, D.J. 1980. Natural organohalogen compounds. In: O. Hutzinger (Editor), The Handbook of Environmental Chemistry. Vol. 1 Part A. The Natural Environment and the Biogeochemical Cycles. Springer-Verlag, Berlin, Heidelberg, New York, pp. 229 - 254.

Goldman, C.R. 1981. Lake Tahoe: two decades of change in a nitrogen deficient oligotrophic lake. Verh. Internat. Verein. Limnol. 21: 45 - 70.

Guildford, S.J., Healey, F.P. & Heckey, R.E. 1987. Depression of primary production by humic matter and suspended sediment in limnocorral experiments at Southern Indian Lake, Northern Manitoba. Can. J. Fish. Aquat. Sci. 44: 1408 - 1417.

Harper, D.B. 1985. Halomethane from halide ion - a highly efficient fungal conversion of environmental significance. Nature 315: 55 - 57.

Harper, D.P., Kennedy, J.T. & Hamilton, J.T.G. 1988. Chloromethane biosynthesis in poroid fungi. Phytochem. 27: 3147-3153.

Hartmans, S.,Schmuckle, A., Cook, A.M. & Leisinger, T. 1986. Methyl chloride: naturally occurring toxicant and C-1 growth substrate. J. Gen. Microbiol. 132: 1139 - 1142.

Hasler, A.D. 1947. Eutrophication of lakes by domestic drainage.

Ecology 28: 383 - 395.

Henry, L.H., Suffet, I.H. & Friant, S.L. 1989. Sorption of chlorinated hydrocarbons in the water column by dissolved and particulate organic material.In: I.H. Suffet & P. MacCarthy (Editors), Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C., pp. 159 - 171.

Hirsch, M. & Hutzinger, O. 1989. Naturally occurring proteins from pond water sensitize hexachlorobenzene photolysis. Environ. Sci. Technol. 23: 1306 - 1307.

Hoigne, J.,Faust, B.C., Haag, W.R.,Scully, F.E.Jr & Zepp, R.G. 1989. Aquatic humic substances as sources and sinks of photochemically produced transient reactants. In: I.H.Suffet & P. MacCarthy (Editors), Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C., pp. 363 - 380.

Horvath, R.S. 1972. Microbial co-metabolism and the degradation of organic compounds in nature. Bacteriological Rev. 36: 146-155.

Hulbert, M.H. & Krawiec, S. 1977. Cometabolism: a critique. J. Theoretical Biol. 69: 287 - 291.

Hutchinson S.A. 1971. Biological activity of volatile fungal metabolites. Trans. Br. mycol. Soc. 57: 185 - 200.

International Joint Commission. 1987. Summary report of the workshop on Great Lakes atmospheric deposition. International Joint Commission, Windsor, Ontario, Detroit, Michigan.41 pp.

Jensen, S. 1972. The PCB story. Ambio 1: 123 - 131.

Kaiser, K.L.E. 1974. Mirex: an unrecognized contaminant of fishes from Lake Ontario. Science 185: 523 - 525.

Kaiser, K.L.E. 1978. The rise and fall of mirex. Environ. Sci. Technol. 12: 520 - 528.

Kaminsky, R. & Hites, R.A. 1984. Octachlorostyrene in Lake Ontario: sources and fates. Environ. Sci. Technol. 18: 275 - 279. 1974.

Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10: 833 - 846.

Keith, L.H. & Telliard, W.A 1979. Priority pollutants. I - A perspective view. Environ. Sci. Technol. 13: 416 - 423.

Kile, D.E. & Chiou, C.T. 1989. Water-solubility enhancement of non-ionic organic contaminants. In: I.H.Suffet & P.MacCarthy (Editors), Aquatic Humic Substances : Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C., pp. 131 - 157.

King, G.M. 1988. Dehalogenation in marine sediments containing natural sources of halophenols. Appl.Environ. Microbiol.54: 3079 - 3085.

Kuhn, E.P.& Suflita, J.P. 1989. Dehalogenation of pesticides by anaerobic microorganisms in soils and groundwater - a review. In: Reactions and Movement of Organic Chemicals in Soils. Soil Society of America Special Publication No. 22, pp. 111 - 180.

Larsson, P. & Lemkemeier, K. 1989. Microbial mineralization of chlorinated phenols and biphenyls in sediment-water systems from humic and clear-water lakes. Water Res. 9: 1081 - 1085.

Larsson, P.,Okla, L. & Tranvik, L. 1988. Microbial degradation of xenobiotic, aromatic pollutants in humic water. Appl. Environ. Microbiol. 4: 1864 - 1867.

Lee, R.F.,Valkirs, A.O. & Seligman, P.G. 1989. Importance of microalgae in the biodegradation of tributyltin in estuarine waters. Environ. Sci. Technol. 23: 1515 - 1518.

Leppard, G.G., Massalski, A. & Lean, D.R.S. 1977. Electron-opaque microscopic fibrils in lakes: their demonstration, their biological derivation and their potential significance in the redistribution of cations. Protoplasma 92: 289 - 309.

Liu, D., Carey, J. & Thomson, K. 1983. Fulvic-acid-enhanced biodegradation of aquatic contaminants. Bull. Environ. Contam. Toxicol. 31: 203 - 207.

Lovelock, J.E. 1975. Natural halocarbons in the air and in the sea. Nature 256:193 - 194.

Macalady, D.L., Tranyk, P.G. & Grundel, T.J. 1986. Abiotic reductions of anthropogenic organic chemicals in anaerobic systems: a critical review. In: D.L. Macalady (Editor), Transport and Transformations of Organic Contaminants. J. Contam. Hydrol. 1, 1 - 28.

Maguire, R.J. & Tkacz, R.J. 1989. Potential underestimation of chlorinated hydrocarbon concentrations in fresh water. Chemosphere 19: 1277 - 1287.

Maguire, R.J., Wong,P.T.S. & Rhamey, J.S. 1984. Accumulation and metabolism of tri-n-butyltin cation by a green alga,

Ankistrodesmus falcatus. Can. J. Fish. Aquat. Sci. 41: 537 - 540.

Margalef, R. 1968. Perspectives in Ecological Theory. University of Chicago Press, Chicago and London. 111 pp.

Margalef, R. 1983. Limnologia.Ediciones Omega,Barcelona. 1010 pp.

Mazumder, A.,Taylor, W.D.,McQueen, D.J. & Lean, D.R.S. 1990. Effects of fish and plankton on lake temperature and mixing depth. Science 247: 312 - 315.

Metcalf, R.L. 1973. A century of DDT. J. Agric. Food Chem. 21: 511 - 519.

Morehead, N.R., Eadie, B.J., Lake, B., Landrum, P.F. & Berner, D. 1986. The sorption of PAH onto dissolved organic matter in Lake Michigan waters. Chemosphere 15: 403 - 412

Mudambi ,A.R. & Hassett, J.P. 1988. Photochemical activity of mirex associated with dissolved organic matter. Chemosphere 17: 1133 - 1146.

Neidleman, S.L. & Geigert, J. 1986. Biohalogenation: principles, basic roles and applications. Ellis Horwood Limited,Chichester. Halsted Press: a division of John Wiley & Sons, New York, Chichester, Brisbane, Toronto. 203 pp.

Quirke, J.M.E., Masrei, A.S.M & Eglington, G. 1979. The degradation of DDT and its degradative products by reduced iron(III) porphyrins and ammonia. Chemosphere 8: 151 - 155.

Rasmussen, J.B.,Godbout, L. & Schallenberg, M. 1989. The humic content of lake water and its relationship to watershed and lake morphometry. Limnol. Oceanogr. 34: 1336 - 1343.

Rasmussen, R.A.,Rasmussen, L.E.,Khalil, M.A.K. & Dalluge, R.W. 1980. Concentration distribution of methyl chloride in the atmosphere. J. Geophys. Res. 85: 7350 - 7356.

Rippey, S.R. & Cabelli, V.J. 1989. Use of the thermotolerant Aeromonas group for the trophic state classification of freshwaters. Water Res. 23: 1107 - 1114.

Ross, R.D. & Crosby, D.G. 1973. Photolysis of ethylenethiourea. J. Agric. Food Chem. 21: 335 - 337.

Senesi, N. & Chen, Y. 1989. Interactions of toxic organic chemicals with humic substances. In: Z.Gerstl, Y.Chen, U.Mingelgrin & B.Yaron. (Editors). 1989. Toxic Organic Chemicals in Porous Media. Springer-Verlag, Berlin, pp. 35 - 90.

Singh, H.B.,Salas, L.A. & Stiles, R.E. 1983. Methyl halides in

and over the eastern Pacific. (40 N - 32 S). J. Geophys. Res. 88: 3684 - 3690.

Spindler, M. 1983. DDT: health aspects in relation to man and risk/benefit assessment based thereon. Residue Rev. 90: 1 - 34.

Stevenson, F.J. 1982. Humus Chemistry: Genesis, Composition, Reactions. John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore. 443 pp.

Suffet, I.H. & MacCarthy, P. (Editors). 1989. Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, D.C.

Talling, J.F.,Wood, R.B.,Prosser, M.V. & Baxter, R.M. 1973. The upper limit of photosynthetic productivity by phytoplankton: evidence from Ethiopian soda lakes. Freshwater Biol. 3: 53 - 76.

ten Noever de Brauw M.C. & Koeman, J.H. 1972/1973. Identification of chlorinated styrenes in cormorant tissues by a computerized gas chromatography-mass spectrometry system. Sci. Total Environ. 1: 427 - 432.

ten Noever de Brauw, M.C., Van Ingen,C. & Koeman, J.H. 1973. Mirex in seals. Sci.Total Environ. 2: 196 - 198.

Vollenweider, R.A. 1969. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to phosphorus and nitrogen as factors in eutrophication. OECD Technical Report DAS/CS1/68.27. 159 pp.

Vollenweider, R.A. 1975. Input-output models. With special reference to the phosphorus loading concept in limnology. Schweiz. Zeitschr. Hydrol.37: 53 - 84.

Wainman, B.C. & Lean, D.R.S. In press. Seasonal trends in planktonic lipid content and lipid class. Verh. Internat. Verein. Limnol. 24.

Wetzel, R.G. 1983. Limnology. Second Edition. Saunders College Publishing, Philadelphia. 753 pp.

White, R.H. 1982. Biosynthesis of methyl chloride in the fungus Phellinus pomaceous . Arch. Microbiol. 132: 100 - 102.

Wolfe, N.L. 1990. Perspectives in aquatic redox chemistry: transformations of pollutants in groundwaters and sediments.In: D.L. Macalady (Editor), Chemical Mediation of Pollutant Transport in Aqueous Systems. J. Contam. Hydrol. XX: xx

Wong, P.T.S., Chau, Y.K., Yaromich, J.L. & Kramar, O. 1987.

Bioaccumulation and metabolism of tri- and dialkyllead compounds by a freshwater alga. Can. J. Fish. Aquat. Sci. 44: 1257 - 1260.

Yan, N.D. 1986. Empirical prediction of crustacean zooplankton biomass in nutrient-poor Canadian shield lakes. Can. J.Fish. Aquat. Sci: 43, 788 - 796.

Zepp,R.G. 1988. Environmental photoprocesses involving natural organic matter. In: F.H.Frimmel & R.F. Christman (Editors), Humic Substances and their Role in the Environment. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, pp. 193 -214.

Zepp, R.G., Wolfe, N.L.,Gordon, J.A. & Fincher, R.C. 1976. Light-induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24: 727 - 733.

Zoro, J.A., Hunter, J.M., Eglington, G., & Ware, G.C. 1974. Degradation of p,p'-DDT in reducing environments. Nature 247: 235 - 237.

NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

Environment Canada Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

Think Recycling!

Pensez à Recycling!