CHAPTER 12

Toxic Effects of Pollutants on Plankton

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12.1. INTRODUCTION

There are four main sources of aquatic pollution: industrial wastes, municipal wastes, agricultural run-off, and accidental spillage. Non-point sources, such as automobile exhausts, add appreciable amounts of pollutants to air that may enter aquatic systems in rainfall or dry fall-out. These sources add pesticides, heavy metals, oil, petroleum products, and a large number of organic and inorganic compounds to water. Lakes and oceans serve as sinks for many pollutants. Plankton comprise a large portion of the living matter in natural waters and function in biogeochemical cycles. They are affected by pollutants, transfer them to sediments and other organisms, and function in their biological transformation.

In natural waters, such as oceans, lakes, rivers, and swamps the greatest amount of biological production is done by the smallest organisms, the plankton. These microscopic plants and animals comprise communities that drift aimlessly with tides and currents, yet they incorporate and cycle large amounts of energy that they pass on to higher trophic levels. Thus communities of plankton, as distinct as those of swamp, forest, or grassland, support other communities of aquatic species and man.

In this chapter, pollution is considered as it affects plankton communities and species. Plankton (Gr. 'wandering') is a general term for those organisms that drift or swim feebly in the surface water of ponds, lakes, streams, rivers, estuaries, and oceans. It is composed of organisms with chlorophyll (phytoplankton) and animals (zooplankton). Phytoplankton is the primary producer community and consists mainly of algae such as diatoms, dinoflagellates, and a variety of forms from other divisions of the plant kingdom. The zooplankton contains consumer species from

Name	Linear dimensions	Organisms		
Megaloplankton	1 cm	Squids, salps		
Macroplankton	1 mm - 1 cm	Large zooplankton		
Mesoplankton	0.5-1.0 mm	Small zooplankton, large diatoms		
Microplankton	0.06-0.5 mm)	Most phytoplankton		
Nannoplankton	0.005-0.06			
Ultraplankton 0.0005-0.005 mm		Bacteria, flagellates		

Table 12.1 Size Classes of Plankton. (Reproduced by permission of the International Council for the Exploration of the Sea, from Cushing *et al.*, 1958)

all major groups of animals except sponges, bryozoans, brachiopods, ascidians, and mammals (Johnson, 1957).

Plankton is composed of algae and animals in various stages of development. All life stages of holoplanktonic species are completed in the plankton, whereas only a portion of the life cycles of meroplanktonic species occurs in plankton. Planktonic forms are relatively small in size and often lack locomotory organs. Size classes are given in Table 12.1. These classes are often referred to in the scientific literature.

Plankton shares space with swimming animals known collectively as 'nekton' (Gr. 'swimming'). Together, plankton and nekton form the pelagic community, that community associated with open water and not with shore or bottom.

Since many pollutants occur in surface waters, plankton functions are likely to be affected by them. Plankton communities generally exhibit cyclical stability, that is, they vary in composition in relation to changes in light, temperature, and availability of nutrients. Relationships between producers and consumers are determined by:

- (1) numbers of each;
- (2) efficiency with which energy is incorporated by algae;
- (3) the rate of renewal of dominant populations;
- (4) the ability of producers to renew consumed production;
- (5) the relationship between energy required for maintenance and that available for production in the dominant species (Schwarz, 1975).

All these involve relationships between populations within the plankton community and regulate, to a large extent, those functions that determine the biological characteristics of natural aquatic systems.

At the ecosystem level, natural water bodies may be described by the properties given in Table 12.2. These properties are associated with rates of energy utilization, nutrient cycling, predator—prey relationships, and size of the energy reservoir within the system. A pollutant that affects any one of them can affect the others in relation to the resiliency of the system.

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Table 12.2 Metabolic Properties that can be Used to Characterize Ecosystems. (Reprinted, with permission from Reichle, 1975, *Bioscience*, published by the American Institute of Biological Science)

Property	Symbol		
Gross Primary Production	GPP		
Autotrophic Respiration	RA		
Net Primary Production	NPP		
Heterotrophic Respiration	R _H		
Net Ecosystem Production	NEP		
Ecosystem Respiration	R _E		
Production Efficiency	R _A /GPP		
Effective Production	NPP/GPP		
Maintenance Efficiency	R _A /NPP		
Respiration Allocation	R_H/R_A		
Ecosystem Productivity	NEP/GPP		

Some systems can restore themselves quickly after being perturbed by adjusting community structure or population function. Others are less resilient to environmental change and disappear, leading to a series of developmental changes that results in a stable community under the new conditions. Although composition of the community changes, species diversity may or may not change because stability is a function of community history and is not related to diversity. Therefore, species diversity, by itself, is not necessarily a good indicator of pollution effects on plankton.

There is a large scientific literature dealing with the effects of pollutants on planktonic species of fresh and marine waters. Much less has been reported about effects on communities and ecosystems. Mathematical models can be used to predict the effects of pollution on plankton communities, and a few simple models will be used here to suggest possible effects of selected pollutants.

12.2. PHYTOPLANKTON

Many studies on algal species and specific pollutants have been published. Most have described effects upon population growth or photosynthesis and indicate that, generally, algae are as sensitive to pollutants as animals. Growth and photosynthesis are closely related, each being a function of the utilization of light and nutrients. Dugdale (1975) described the growth of an algal population as being proportional to the effect of light on photosynthesis (Ryther, 1956; Yentsch, 1974), the concentration of nutrients, and the maximum specific growth rate. Pollutants can affect the relation between growth rate and each of these variables. For example, if an industrial effluent is coloured or contains suspended solids, light may be filtered

or absorbed by it, resulting in a reduced growth rate. MacIsaac and Dugdale (1976) demonstrated that reduction of light caused reduction in rate of uptake of ammonia and nitrate by marine phytoplankton.

Some chemicals interfere with the Hill reaction of photosynthesis. The Hill reaction is a light-dependent transfer of electrons from cell water to nicotinamide adenine dinucleotide phosphate (NADP) and is inhibited by such compounds as triazines, ureas, carbamates, and acylanilides. Thus chemical pollutants can also block the effect of light on the photosynthetic mechanism and inhibit growth. Walsh (1972) demonstrated that, in four species of marine algae, the EC_{50} 's (concentrations that reduced rate of growth or rate of oxygen evolution by 50%) for Hill reaction inhibitors such as ametryne, atrazine, and diuron were approximately the same for growth and rate of photosynthesis. There was no such correlation between compounds such as silvex, diquat, and trifluralin that had other modes of action (Table 12.3). Overnell (1975) showed that light-induced oxygen evolution from the freshwater species Chlamydomonas reinhardii was very sensitive to cadmium, methylmercury, and lead. Moore (1973) found that organochlorine compounds reduce utilization of bicarbonate by estuarine phytoplankton. See the review of Whitacre et al. (1972) for effects of many chlorinated hydrocarbons on carbon fixation by phytoplankton.

Pollutants can, therefore, affect photosynthesis and other aspects of energy utilization and incorporation and, thus cause changes in population growth rates. Such changes are most easily seen in systems polluted by algal and plant nutrients. Although there does not seem to be any consistent relationship between nutrient concentrations and biomass of phytoplankton, the rate of autotrophic production of a system may be regulated to a great extent by pollutants (Table 12.4). Goldman (1974), in an extensive study of the eutrophication of Lake Tahoe, found that nitrogen, iron, and phosphorus had a great effect on the rate of primary productivity. He also demonstrated that the rate of primary productivity increased markedly between 1959 and 1971 (Table 12.5). Measurements of primary productivity together with measurements of heterotrophy were the most sensitive indicators of eutrophication in the lake. Measurement of change in the rate of photosynthesis over a number of years may be a sensitive method for the detection of pollution by nutrients.

Pollutants may also affect species composition of the plankton community. Eutrophic systems commonly contain mainly blue-green algae (Cyanophyta), especially in summer (Walsh, 1975), although they do not seem to be more sensitive to pollutants than other algae (Fitzgerald *et al.*, 1952; Whitton, 1970; Venkataraman and Rajyalakshmi, 1971; Voight and Lynch, 1974; DaSilva *et al.*, 1975). Walsh (1975) showed that, in four coastal ponds, cyanophytes comprised nearly 100% of the total algal number, and that the ratio of photosynthesis to respiration was as high as 2.7, indicating a very high productivity. The reason for blooms of cyanophytes is not known, but they often occur after blooms of green algae (Chlorophyta). When cyanophytes begin to grow, the water often contains

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Table 12.3 EC₅₀ Values (parts per million) for Growth and Photosynthesis (rate of oxygen evolution) by Four Genera of Marine UniceHular Algae when Exposed to Hill Reaction Inhibitors (ametryne, atrazine, and diuron) and Non-Hill Reaction Inhibitors (silvex, diquat, and trifluralin). (Reproduced by permission of the Editor, *Hyacinth Contr. J.* from Walsh, 1972).

	Chlorococo	cum	Dunaliella		Isochrysis		Phaeodactylum		
Herbicide	growth	photo.	growth	photo.	growth	photo.	growth	photo	
Ametryne	0.01	0.02	0.04	0.04	0.01	0.01	0.02	0.01	
Atrazine	0.10	0.10	0.30	0.30	0.10	0.10	0.20	0.10	
Diuron	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.02	
Silvex	25	250	25	200	5.0	250	5.0	300	
Diquat	200	5,000	30	5,000	15	5,000	15	5,000	
Trifluralin	2.5	500	5.0	500	2.5	500	2.5	500	

Table 12.4 Rates of Phytoplankton Production in Oligotrophic and Eutrophic Lakes. (Reproduced by permission of the National Academy of Sciences from Rodhe, 1969)

Type of lake	Rate of production (g C/m ² /yr)
Oligotrophic	7-25
Natural eutrophic	75-250
Polluted eutrophic	350-700

only small amounts of nitrogen and phosphorus. Fogg *et al.* (1973) described the ability of cyanophytes to fix nitrogen, and this could give them a competitive advantage when nitrogen is in very low concentration. Also, blue-green algae require sodium and potassium, the optimum being 2.5 to 5.0 ppm in water (Emerson and Lewis, 1942). These elements are often found in the required concentrations in polluted waters, a fact that led Provasoli (1958) to suggest that their presence is a factor that selects cyanophytes over chlorophytes.

Lund (1969) suggested that, since cyanophytes are seldom grazed upon by herbivores, they have a competitive advantage over chlorophytes which are grazed upon. Talling (1965) suggested that blue-green algae are not harmed by high temperature and intense illumination in summer and that they may be selected because of this adaptation.

Davies (1976) measured the effect of Hg^{2+} on the specific growth rate of *Dunaliella tertiolecta*, a marine alga, in culture. The specific growth rates of control and treated cultures with up to 2.03 micromolar Hg^{2+} varied between 0.65 and 0.70. At 5.02 micromolar Hg^{2+} it was 0.43, and at 10.0 micromolar Hg^{2+} it was 0.11. At 10.0 micromolar Hg^{2+} , growth was uncoupled from cell division and giant cells were produced. Davies suggested that growth without division was due to

Table 12.5 Total Primary Productivity of Phytoplankton per Year in Lake Tahoe. (Reproduced by permission of the United States Environmental Protection Agency from Goldman, 1974)

Year	Productivity (mg·C/m ² /yr)	Percentage increase from 1959			
1959	38,958				
1968	46,685	20			
1969	50,525	30			
1970	52,467	35			
1971	58,655	51			

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inhibition of methionine production by mercury. It is important, therefore, when testing for effects of some pollutants, that total volume or weight of living matter be measured, and not only cell numbers.

Algal growth may be inhibited or stimulated by pollutants that affect nutrient relationships. The mechanisms whereby they affect the chemical state of a nutrient or its uptake and utilization vary according to nutrient, physical and chemical conditions of the water, and algal species. Meijer (1972) showed that a decrease in the phosphate concentration in the growth medium caused an increase in toxicity of copper to Chlamydomonas sp. as measured by oxygen production and an increase in cell numbers. There was a strong effect of 2 mg PO₄/l at the very high concentration of 2 mg Cu/l. Steeman-Nielsen et al. (1969) reported similar results and suggested that the toxic effect of copper is due to binding to the cytoplasmic membrane, thus arresting cell division. Zarnowski (1972) demonstrated this to be true with iron and Chlorella pyrenoidosa and stated that phosphorus compounds cause oxidation and precipitation of iron from water. Sheih and Barber (1973) showed that mercury in low concentration (0.03 mM HgCl₂) as mercuric chloride stimulated the rate of potassium turnover in C. pyrenoidosa but did not affect the concentration of internal potassium. At higher concentrations (0.5 mM HgCl₂) mercury caused changes in permeability of the cell membrane that resulted in a net efflux of potassium.

The stimulatory effect of low concentrations of heavy metals on algae is well known. DeFilippis and Pallaghy (1976) hypothesized that 1 mM ZnCl_2 , $1 \mu \text{M}$ HgCl₂, or $0.1 \mu \text{M}$ phenylmercuric acetate stimulated growth by preventing loss of carbon compounds from *Chlorella* sp. They suggested that heavy metals either interfere with production of glycollate or inhibit its secretory mechanism.

Such actions by heavy metals are often related to ionic state. In sediments at low redox potential, Hg^{2+} is reduced to Hg^0 with the formation of dimethylmercury by methyl radical addition. Organic mercurial compounds are sometimes more toxic than inorganic compounds. Harriss *et al.* (1970) showed that 0.1 ppb (μ g/l) of methylmercury reduced photosynthesis (as ¹⁴ C uptake) and growth of the marine diatom *Nitzschia delicatissima*. However, dimethylmercury was less toxic; 1 ppb was required for an effect. The authors stated that the alga was sensitive to much lower concentrations of mercurial compounds than fishes. Davies (1976) suggested that some algae detoxify mercury by reduction of Hg^{2+} to Hg^+ in the outer layers of the cell. Zingmark and Miller (1975) noted that net photosynthesis by *Amphidinium carteri* was decreased 92% by 100 ppb mercury. However, Hg^{2+} was reduced to Hg^0 during the test.

A very important aspect of uptake and toxicity of heavy metals to phytoplankton is the role of chelating agents. Plum and Lee (1973) showed that up to 20% of the iron in a lake was associated with organic matter. Andren (1973) found that mercury in the water of three estuaries was associated with dissolved organic matter. Dissolved mercury was associated with dissolved organic matter of the humic and fulvic types. In a Norwegian lake, Beneš *et al.* (1976), showed that sodium, calcium, aluminium, chromium, iron, zinc, manganese, mercury, and other elements were bound strongly to humus. Slowey *et al.* (1967) indicated that up to 50% of the total copper present in sea water from the Gulf of Mexico was complexed with phospholipid, amino lipid, or porphyrin fractions. The samples were taken from the sea surface, and the authors speculated that the organic compounds were present because of rupture of fragile planktonic organisms.

Perdue *et al.* (1976) described competition between metals for binding sites on dissolved organic matter; thus iron, for example, may be present in water as (1) free colloidal particles of iron hydroxide, possibly associated with colloidal organic matter, and (2) dissolved complexes of iron with naturally occurring organic substances. The authors gave evidence that aluminium competes with iron for sites on molecules of dissolved organic matter. Hendrickson *et al.* (1974) demonstrated the high affinity of cadmium for dissolved organic matter from a lake in Wisconsin.

Formation of chelates implies that the amount of dissolved matter may, in some cases, regulate toxicity of metals because chelation decreases toxicity to a very great extent. Lomonosov (1969) showed that copper dichloride pyridinate inhibited growth of *Scenedesmus quadricauda* at 0.4 mg Cu/l. Copper chelates were much less toxic. Walsh *et al.* (unpublished) have found that when the marine unicellular alga *Dunaliella tertiolecta* is exposed to nickel in the presence of the chelator ethylenediaminetetraacetic acid (EDTA) its EC₅₀ was 9.1 ppm. When EDTA was excluded from growth media the EC₅₀ was 2.4 ppm.

They have also found (unpublished) that the herbicide 2,4-D inhibits the toxicity of nickel and aluminium. One type of interaction between pollutants can be formulated by the expression (Colby, 1967)

$$E = \frac{XY}{100} \tag{12.1}$$

where

- E = expected population density of algae as a percentage of the control
- X = population density as a percentage of the control when exposed to chemical X

Y = population density as a percentage of the control when exposed to chemical Y

When the observed value of E is less than the expected value, the combination acts synergistically; when equal, the combination acts additively; when greater, the interaction is antagonistic. Table 12.6 shows that nickel and 2,4-D react antagonistically; therefore, in evaluating effects of pollutants on algae, it is necessary to consider the chemical nature of dissolved materials, including other pollutants.

In other types of interactions, Tsay *et al.* (1976) demonstrated that copper ions (2 ppm) inhibited toxicity of the insecticide paraquat (1,1-dimethyl-4,4'-bipyridinum ion, 2 ppm) to *C. pyrenoidosa*, whereas cyanide ion (16 ppm)

	Chloro	coccum	Dunali	ella	Thalassiosira		
Concentration	calc.	obs.	calc.	obs.	calc.	obs.	
1 ppm Ni + 50 ppm 2,4-D	84.0	84.5	79.6	98.9	30.2	35.8	
2 ppm Ni + 50 ppm 2,4-D	55.9	75.9	64.3	96.0	29.7	37.6	
4 ppm Ni + 50 ppm 2,4-D	34.9	63.8	53.6	88.6	13.9	36.4	

Table 12.6 Calculated and Observed Values of E (equation 12.1) for Three Genera of Marine Unicellular Algae Exposed to Nickel (as NiCl₂) and the Technical Acid of 2,4-D (Walsh, unpublished)

enhanced herbicide activity. The toxic effects of phenylurea herbicides to *Chlorella vulgaris* were shown by Kruglov and Kvyatkovskaya (1975) to be inversely related to the humus content of the soil.

It is clear, therefore, that many pollutants exert their effects in relation to the uptake dynamics of nutrients, heavy metals, carbon, etc. The dynamics of such uptake are explained by the expressions of Volterra (1926):

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = N_1 \left[\epsilon_1 - r_1 (h_1 N_1 + h_2 N_2) \right]$$
(12.2)

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = N_2 \left[\epsilon_2 - r_2 (h_1 N_2 + h_2 N_2) \right]$$
(12.3)

where

 N_1, N_2 = numbers of two competing species

 ϵ_1, ϵ_2 = their coefficients of increase with unlimited nutrient

 r_1, r_2 = constants of susceptibility to nutrient shortage

 h_1, h_2 = constants of nutrient consumption.

The equations are based on the assumptions that

- (1) rate of depletion of a nutrient pool is directly proportional to size of the population;
- (2) depletion of the pool reduces the growth rate;
- (3) the coefficients of increase, which are related to efficiency of utilization of nutrients, are different for each species.

The equation predicts dominance of one species over others; i.e. the species that is most susceptible to the influence of pollution will be eliminated in competition with a species of lesser susceptibility.

Dominance is determined by many factors, and, for any given species, may be related to temperature, salinity, irradiation, pollution, etc. Mandelli (1969) reported that the growth of selected species of dinoflagellates and diatoms was inhibited by copper between 0.055 and 0.256 μ g/ml. However, there was a positive

correlation between the log of the ratio of copper uptake, biomass of algae and temperature, but a negative correlation between that ratio and salinity. Walsh and Grow (1971) demonstrated a direct correlation between carbohydrate concentration in algal cells and concentration of urea herbicides in the growth medium.

If it is assumed that the coefficients of increase of different species are affected in different ways by pollutants in relation to environmental conditions, then changes in species composition of a community are to be expected. Such differences were shown by Hollister and Walsh (1973) who reported the responses of 18 species of marine unicellular algae to four compounds that inhibit the Hill reaction. There were large differences in the coefficients of increase among the species. Bowes (1972) reported that 80 μ g/l of DDT had no effect on growth of the marine alga Dunaliella tertiolecta, had slight effect on growth of Cyclotella nana, Thalassiosira fluviatilis, Amphidinium carteri, Coccolithus huxleyi, and Porphyridium sp., but caused a lag of nine days in growth of Skeletonema costatum. Fisher et al. (1973) showed that estuarine clones of the algae Thalassiosira pseudonana, Fragilaria pinnata, and Bellerochia sp. were more resistant to PCBs (polychlorinated biphenyls) than were oceanic clones. Dunstan et al. (1975) demonstrated effects of oil on marine phytoplankton and concluded that a significant effect of oil could be the stimulation of some species by aromatic compounds of low molecular weight, resulting in the alteration of natural phytoplankton community structure and its trophic relationships. These works suggest that, in mixed culture, the competitive exclusion principle of Gause (1934) would operate, causing species best adapted to the polluted condition to dominate.

Changes in structure of a marine algal community under stress from PCBs and DDT were demonstrated by Mosser *et al.* (1972) and Fisher *et al.* (1974). In untreated mixed cultures, *T. pseudonana* was dominant in number over *D. tertiolecta*. When treated with 1 ppb of PCBs or 10 ppb of DDT, the competitive success of *T. pseudonana* decreased while that of *D. tertiolecta* increased, even though the pollutant concentration had no effect on *T. pseudonana* in pure culture.

Another important aspect of pollution is the fact that algae accumulate many compounds and heavy metals by absorption or by adsorption to the cell wall. In general, pollutants such as pesticides are not degraded to a large extent by algae (Butler *et al.*, 1975) and are passed on to herbivores when eaten. Hollister *et al.* (1975) showed that four species of marine phytoplankton, when exposed to only 10 pptr (parts per trillion) of the insecticide mirex, concentrated it to over 100 ppb (parts per billion) on cells. Numerous other publications report uptake of pollutants by phytoplankton (Falchuk *et al.*, 1975; Stokes, 1975; DeFilippis and Pallaghy, 1976; Glooschenko and Lott, 1976).

Uptake and accumulation of substances may prove to be the most important aspect of phytoplankton pollution dynamics. Since they are grazed upon by many animals, the phytoplankton may be a vital link in the transfer of pollutants from water to higher trophic levels, including man.

12.3. ZOOPLANKTON

Zooplankton comprise a very dynamic portion of the total plankton. There is greater species diversity among the zooplankton than phytoplankton, and composition varies strongly with seasonal production of meroplankton such as medusae, eggs, larvae, and juveniles of the benthos and nekton. Functionally, the zooplankton includes detritivores, herbivores, carnivores, and omnivores, all of which excrete dissolved and particulate organic and inorganic materials that can serve as nutrients for saprovores, phytoplankton, and coprovores. Organic and inorganic materials are lost from the water column when organisms die and settle to the bottom, where they enter geochemical cycles involving sediments.

Zooplankton population production is a function of the intrinsic rate of increase, natural mortality, mortality due to pollution, and rate of predation:

Rate of increase	Rate of change in the absence	Rate of	Rate of loss
of population =	of predators and pollution	predation	due to effects
			of pollution

It is difficult to measure an effect of pollution on the rate of predation, but such an effect is theoretically probable. For example, if a compound such as chlorinated hydrocarbon insecticide were present, it could affect the efficiency of a prey arthropod to avoid a predatory fish. Since arthropods are generally more sensitive to the direct influence of such pollutants than fishes, their rates of population increase could be expected to decline because of increased predation and direct mortality due to insecticide.

Hansen (1974) studied the effect of 'Aroclor' 1254, a polychlorinated biphenyl (PCB), on settling of planktonic larvae (meroplankton). He used the composition of estuarine animal communities that developed while meroplankton were subjected to three concentrations of the pollutant for four months. Arthropods constituted over 75% of the organisms in untreated aquaria and aquaria that received $0.1 \,\mu g/l$ of PCB. Two other aquaria that received 1.0 and $10 \,\mu g/l$ were dominated by chordates, primarily tunicates. Just as important, however, is the fact that species diversity, as measured by the Shannon-Weaver index (Shannon and Weaver, 1963), was not affected, indicating that such an index cannot always measure pollution effects on planktonic larvae.

Conversely, temporal changes in zooplankton community composition may be modified if benthic and nektonic contributions to the meroplankton are affected by pollution. Numerous reports show that zooplanktonic species and meroplanktonic larvae are often much more sensitive to pollutants than adults. Armstrong and Millemann (1974) showed that, for the mussel, *Mytilus edulis*, the developmental stage most sensitive to the insecticide 'Sevin' occurred shortly after fertilization, at the time of appearance of the first polar body. Sensitivity decreased in each succeeding stage. The EC₅₀ of 'Sevin' at the first polar body stage was 5.3

ppm. At the 32-hr stage, the EC_{50} was 24.0 ppm. Affected eggs were characterized by dysjunction of blastomeres, reduction in rate of development, and asynchronous and unaligned cleavages. Bookhout and Costlow (1976) demonstrated that certain zoeal stages of the crabs Callinectes sapidus and Rhitropanopeus harrisii were the most sensitive to the insecticides mirex, methoxychlor, and malathion, and that the total time from hatching to the first crab stage was prolonged by methoxychlor and malathion. The total time of larval development of the crabs, Menippe mercinaria and R. harrisii, was lengthened by 0.01 to 10.0 ppb of mirex. Crabs that had been reared in 0.1 ppb of mirex concentrated it 2,400 times in their bodies (Bookhout et al., 1972). Rosenberg (1972) found reduction in the swimming activity of stage II nauplii of the barnacle, Balanus balanoides, by 2 ppm of chlorinated aliphatic hydrocarbons. Stages V and VI were affected by 4 ppm. Young juvenile mullet, Mugil cephalus, were more susceptible to mirex exposure than older juveniles or adults (Lee et al., 1975), and cadmium reduced the incubation time (50% hatching time) of herring (Clupea harengus) eggs. Conversely, Bills (1974) reported that formalin and malachite green were more toxic to rainbow trout, Salmo gairdneri, fingerlings than to the eved egg stage.

Generally, greater susceptibility of young to pollutants could have a strong effect upon all factors that determine the rates of increase of prey and predator species. Also, change in the carrying capacity of herbivorous zooplankton could affect the carrying capacity for phytoplankton.

Reduced stocks of young that survive to maturity could greatly affect the size of a reproductive population. For example, temporal extension of larval stages or weakening of young would make them vulnerable to excessive predation and ultimately reduce the size of the reproducing population during the next production year. Nimmo *et al.* (in press), using the mysid *Mysidopsis bahia*, found a 24-hour delay in the formation of brood pouches and reduced production of young by females exposed to $6.4 \mu g$ Cd/l.

Adult zooplankton are affected by pollutants and accumulate relatively large amounts. Uptake can occur either through ingestion of contaminated food or directly from water. When Burnett (1973) fed a marine copepod, *Tigriopus* sp., phytoplankton exposed to DDE, growth rate and egg production were reduced. Maki and Johnson (1975) demonstrated reproductive inhibition in the freshwater species, *Daphnia magna*, by DDT and a commercial formulation of PCBs. Reproduction was inhibited by 0.30 ppb of DDT and 10.0 ppb of PCB. In static toxicity tests that used survival as the criterion of effect, the LC₅₀ s were 0.67 ppb for DDT and 24.0 for PCB. Thus the EC₅₀ based on the number of young produced was approximately one-half of the EC₅₀ based on survival. Baudouin and Scoppa (1974) compared the responses of several species of freshwater zooplankton to twelve heavy metals and concluded that members of the genus *Daphnia* were considerably more sensitive than were copepods. They recommended that this genus be used in toxicity tests with metals. Khan and Khan (1974) showed that *Daphnia* accumulated larger amounts of photodieldrin than other aquatic invertebrates. Its magnification ratio (concentration in animal/concentration in water) was 63,000 when exposed to 6 ppb. Body residues were greatest when contaminated algae were fed to *Daphnia pulex* (Khan *et al.*, 1975) but up to 70% of the pollutant was depurated in 2 days. Dieldrin and photodieldrin were not metabolized (Neudorf and Khan, 1975).

Varying sensitivities to pollutants among zooplankton species could cause changes in community structure by affecting variables such as rate of increase, rate of predation, mortality, and population density. This situation was demonstrated by Sprules (1975) who showed that major changes in composition of crustacean zooplankton communities of acid-stressed lakes were related to pH. Industrial acidification caused decreases in the number of species and changes in species dominance, both of which were affected as pH fell from 7.0 to 3.8.

In general, zooplankton do not degrade pesticides to a great degree. Sameoto *et al.* (1975) reported 68 to 1,757 ppb DDT and 24 to 937 ppb DDE in the lipids of three species of euphausiids in Canada. No other metabolites were found. Darrow and Harding (1975) were unable to demonstrate metabolic products of DDT in marine copepods, but Burnett (1973) stated that DDT was converted to DDE in the marine copepod, *Tigriopus*. In fresh water, DDT was converted to DDE by *Daphnia pulex* (Neudorf and Khan, 1975).

Lee (1975) reported that marine copepods, euphausiids, crab zoea, ctenophores, and jelly-fish rapidly took up benzpyrene, methyl cholanthrene, and naphthalene from sea-water solution. They were metabolized to various hydroxylated and more polar metabolites by the crustaceans but not by ctenophores or jelly-fish. Four species of copepods depurated the hydrocarbons, but depuration was never complete.

12.4. RECOMMENDATIONS

There are many models for explaining and predicting the effects of pollutants on the ecosystem dominated by plankton, and these models may serve as hypotheses for planning research. There is a lack of data for verification of the present models and for generation of new, more accurate models.

At the species level, data are needed with regard to effects of pollution on species composition of plankton communities, and this implies understanding of effects on single species. At present, it is impossible to predict effects on communities from data on single species because little is known about the requirements under conditions of competition, for temperature, salinity, maximal energy utilization, and other physiological and ecological considerations.

We need to know more about lethal and sublethal effects of pollutants on geographical variants of single species. Oceanic clones tend to be more susceptible than estuarine clones. The reason for this is not known, though it may rest in genetic differences. Pollutants can affect nucleic acids within cells, and it would be beneficial to know the genetic basis of tolerance. At the ecosystem level, data on pollution and the basic functions listed in Table 12.2 are needed. Studies on nutrient cycling may lead to the development of sensitive methods for detection of sublethal effects. Possible uses of artificial ecosystems should be investigated in this regard.

Mathematical and conceptual models must be developed to explain the effects of pollution on structure and function of populations and communities and their physical, chemical, and biological environments.

Basic marine microbial ecology requires study. Information on microbial population structure, species successions, and interactions must be obtained. Very few data are presently available.

The interactive and sequential events occurring in microbial degradation of oil and other pollutants must be clearly understood. For example, at present, the succession of groups of microorganisms in mixed cultures degrading petroleum hydrocarbons is only partially understood (see Chapter 13). The mechanisms of biodegradation *in situ*, such as co-metabolism, have not been sufficiently studied so that the biodegradative events that follow microbial seeding of spills cannot be predicted with accuracy.

The action of microorganisms in the production and accumulation of carcinogenic compounds in the marine environment needs to be elucidated.

The role of microorganisms, i.e. the bacteria, yeasts, and fungi, in the marine food chains must be elucidated, since amplification of carcinogenic compounds may occur and, thereby, pose more serious environmental problems.

12.5. REFERENCES

- Andren, A. W., 1973. The geochemistry of mercury in three estuaries from the Gulf of Mexico. *Ph.D. Dissertation*, University of Florida, Gainesville, 140 pp.
- Armstrong, D. A. and Millemann, R. E., 1974. Effects of the insecticide 'Sevin' and its first hydrolytic product, 1-naphthol, on some early developmental stages of the bay mussel *Mytilus edulis*. Mar. Biol. (Berl.), 28, 11-5.
- Baudouin, M. F. and Scoppa, P. S., 1974. Acute toxicity of various metals to freshwater zooplankton. *Bull. Environ. Contam. Toxicol.*, 12, 745-51.
- Beneš, P., Gjessing, E. T., and Steinnes, E., 1976. Interactions between humus and trace elements in freshwater. *Water Res.*, 10, 711–6.
- Bills, T. D., 1974. Toxicity of formalin, malachite green, and the mixture to four life stages of rainbow trout. M.Sc. Thesis, University of Wisconsin, La Crosse, 41 pp.
- Bookhout, C. G. and Costlow, J. D., 1976. Effects of mirex, methoxychlor, and malathion on development of crabs. U.S. Environmental Protection Agency, Pub. No. EPA-600/3-76-007, Gulf Breeze, Florida, 85 pp.
- Bookhout, C. G., Wilson, A. J. Jr., Duke, T. W., and Lowe, J. I., 1972. Effects of mirex on the larval development of two crabs. Water, Air, Soil Pollut., 1, 165-80.
- Bowes, G. W., 1972. Uptake and metabolism of 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) by marine phytoplankton and its effect on growth and electron transport. *Plant Physiol*, **49**, 172-6.

- Burnett, R. D., 1973. DDT in marine phytoplankton and crustacea. Diss. Abstr. Int. B. Sci. Eng., 34, 533.
- Butler, G. L., Deason, T. R., and O'Kelley, J. C., 1975. Loss of five pesticides from cultures of twenty-one planktonic algae. *Bull. Environ. Contam. Toxicol.*, 13, 149-52.
- Colby, R. S., 1967. Calculating synergistic and antagonistic responses of herbicide combinations. Weeds, 15, 20-2.
- Cushing, D. H., Humphrey, G. F., Banse, K., and Laevastu, T., 1958. Report of the committee on terms and equivalents. In *Measurements of Primary Production in the Sea*, Coun. Perm. Internat. Explor. Mer, Copenhagen, pp. 15-16.
- Darrow, D. C. and Harding, G. C. H., 1975. Accumulation and apparent absence of DDT metabolism by marine copepods, *Calanus* sp., in culture. J. Fish. Res. Bd. Canada, 32, 1845-9.
- DaSilva, E. J., Henriksson, L. E., and Henriksson, E., 1975. Effect of pesticides on blue-green algae and nitrogen-fixation. Arch. Environ. Contam. Toxicol., 3, 193-204.
- Davies, A. G., 1976. An assessment of the basis of mercury tolerance in *Dunaliella* tertiolecta, J. Mar. Biol. Assoc. U.K., 56, 39-57.
- DeFilippis, L. F. and Pallaghy, C. K., 1976. The effect of sublethal concentrations of mercury and zinc on *Chlorella*. I. Growth characteristics and uptake of metals. Z. *Pflanzenphysiol.*, 78, 197-207.
- Dugdale, R. C., 1975. Biological modelling I. In Modelling of Marine Systems (Ed. J. C. J. Nihoul), Elsevier Pub. Co., New York, pp. 187-205.
- Dunstan, W. M., Atkinson, L. P., and Natoli, J., 1975. Stimulation and inhibition of phytoplankton growth by low molecular weight hydrocarbons. *Mar. Biol.*, 31, 305-10.
- Emerson, R. and Lewis, C. M., 1942. The photosynthetic efficiency of phycocyanin in *Chroococcus* and the problem of carotenoid participation in photosynthesis. J. Gen. Physiol., 25, 579-95.
- Falchuk, K. H., Fawcett, D. W., and Vallee, B. L., 1975. Role of zinc in cell division of Euglena gracilis. J. Cell. Sci., 17, 57-8.
- Fisher, N. S., Carpenter, E. J., Remsen, C. C., and Wurster, C. F., 1974. Effects of PCB on interspecific competition in natural and gnotobiotic phytoplankton communities in continuous and batch cultures. *Microbiol. Ecol.*, 1, 39–50.
- Fisher, N. S., Graham, L. B., Carpenter, E. J., and Wurster, C. F., 1973. Geographic differences in phytoplankton sensitivity to PCBs. *Nature*, 241, 548–9.
- Fitzgerald, G. P., Gerloff, G. C., and Skoog, F., 1952. Studies on chemicals with selective toxicity to blue-green algae. *Sewage Indust. Wastes*, 24, 888-96.
- Fogg, G. E., Stewart, W. D. P., Fay, P., and Walsby, A. E., 1973. *The Blue-Green Algae*, Academic Press, New York, vii, 459 pp.
- Gause, G. F., 1934. The Struggle for Existence, Williams and Wilkins, Baltimore, 163 pp.
- Glooschenko, V. and Lott, J. N. A., 1976. Effects of chlordane on the green alga Scenedesmus quadricauda. Abst. Thirty-ninth Ann. Meeting, Am. Soc. Limnol. Oceanogr., Savannah, Georgia.
- Goldman, C. R., 1974. Eutrophication of Lake Tahoe emphasizing water quality. U.S. Environmental Protection Agency, Ecological Res. Ser., EPA-660/3-74-034, Corvallis, Oregon, xvii, 408 pp.
- Hansen, D. J., 1974. 'Aroclor' 1254. Effect on composition of developing estuarine animal communities in the laboratory. *Contrib. Mar. Sci.*, 18, 19–33.

- Harriss, R. C., White, D. B., and Macfarlane, R. B., 1970. Mercury compounds reduce photosynthesis by plankton. *Science*, **170**, 736-7.
- Hendrickson, D. W., Armstrong, D. E., Veith, G. D., and Glass, G. E., 1974. Nature of organic derivatives of selected toxic metals in natural waters. Univ. Wisconsin, Water Resources Center, Tech. Rep., WIS WRC 74-07, iii, 23 pp.
- Hollister, T. A. and Walsh, G. E., 1973. Differential responses of marine phytoplankton to herbicides: oxygen evolution. *Bull. Environ. Contam. Toxicol.*, 9, 291-5.
- Hollister, T. A., Walsh, G. E., and Forester, J., 1975. Mirex and marine unicellular algae: accumulation, population growth and oxygen evolution. *Bull. Environ. Contam. Toxicol.*, 14, 753-9.
- Johnson, M. W., 1957. Plankton. In Treatise on Marine Ecology and Paleoecology, Vol. I, Ecology (Ed. J. W. Hedgepeth), pp. 443-59, Geol. Soc. Am. Mem. No. 67, vii, 1296 pp.
- Khan, H. M. and Khan, M. A. Q., 1974. Biological magnification of photodieldrin by food chain organisms. *Arch. Environ. Contam. Toxicol.*, **2**, 289–301.
- Khan, H. M., Neudorf, S., and Khan, M. A. Q., 1975. Absorption and elimination of photodieldrin by *Daphnia* and goldfish. *Bull. Environ. Contam. Toxicol.*, 13, 582-7.
- Kruglov, Y. V. and Kvyatkovskaya, L. B., 1975. Algae as indicators of herbicide contamination of soil. *Rocz. Glebozn.*, 26, 145-9.
- Lee, J. H., Nash, C. E., and Sylvester, J. R., 1975. Effects of mirex and methoxychlor on striped mullet, *Mugil cephalus* L. U.S. Environmental *Protection Agency, Pub.*, No. EPA-660/3-75-015, Gulf Breeze, Florida, 18 pp.
- Lee, R. F., 1975. Fate of petroleum hydrocarbons in marine zooplankton. Proc. 1975 Conf. Prevent. Cont. Oil Poll., Am. Pet. Inst., Washington, D.C. pp. 549-53.
- Lomonosov, M. V., 1969. The toxicity of copper complexes towards *Scenedesmus* quadricauda. Mikrobiologiya, 38, 729-31.
- Lund, J. W. G., 1969. Phytoplankton. In *Eutrophication: Causes, Consequences, Correctives*, pp. 306-30. U.S. Nat. Acad. Sci. Washington, D.C., vii, 661 pp.
- MacIsaac, J. J. and Dugdale, R. C., 1976. Inorganic nitrogen uptake by marine phytoplankton under *in situ* and simulated *in situ* incubation conditions: results from the northwest African upwelling region. *Limnol. Oceanogr.*, 21, 149-52.
- Maki, A. W. and Johnson, H. E., 1975. Effects of PCB ('Aroclor' 1254) and p,p'-DDT on production and survival of Daphnia magna Strauss. Bull. Environ. Contam. Toxicol., 13, 412-6.
- Mandelli, E. E., 1969. The inhibitory effects of copper on marine phytoplankton. Contrib. Mar. Sci., 14, 47-57.
- Meijer, C. L. C., 1972. The effect of phosphate on the toxicity of copper for an alga (*Chlamydomonas* sp.) (in Dutch). *TNO-nieuws*, 27, 468-73.
- Moore, S. A., Jr., 1973. Impact of pesticides on phytoplankton in Everglades estuaries. South Florida Environmental Project, Ecological Rep., No. Di-SFEP-74-15, 100 pp.
- Mosser, J. L., Fisher, N. S., and Wurster, C. F., 1972. Polychlorinated biphenyls and DDT alter species composition in mixed cultures of algae. *Science*, 176, 533-5.
- Neudorf, S. and Khan, M. A. Q., 1975. Pick-up and metabolism of DDT, dieldren and photodieldrin by a freshwater alga (Ankistrodesmus amalloides) and a microcrustacean (Daphnia pulex). Bull. Environ. Contam. Toxicol., 13, 443-50.
- Nimmo, D. R., Rigby, R. A., Bahner, L. H., and Sheppard, J. M. The acute and chronic effects of cadmium on the estuarine mysid *Mysidopsis bahia*. Bull. Environ. Contam. Toxicol., 19(1), 80-85.

- Overnell, J., 1975. The effect of some heavy metal ions on photosynthesis in a freshwater alga. *Pestic. Biochem. Physiol.*, 5, 19-26.
- Perdue, E. M., Beck, K. C., and Reuter, J. H., 1976. Organic complexes of iron and aluminum in natural waters. *Nature*, 260, 418-20.
- Plum, R. H., Jr. and Lee, G. F., 1973. A note on the iron-organic relationship in natural water. Water Res., 7, 581-5.
- Provasoli, L., 1958. Nutrition and ecology of protozoa and algae. Ann. Rev. Microbiol., 12, 279-308.

Reichle, D. E., 1975. Advances in ecosystem analysis. *BioScience*, 25, 257-64.

- Rodhe, W., 1969. Crystallization of eutrophication concepts in northern Europe. In Eutrophication: Causes, Consequences, Correctives, pp. 50-64, U.S. Nat. Acad. Sci. Washington, D.C., vii, 661 pp.
- Rosenberg, R., 1972. Effects of chlorinated aliphatic hydrocarbons on larval and juvenile *Balanus balanoides*. *Environ. Pollut.*, **3**, 313-8.
- Ryther, J. H., 1956. The measurement of primary production. *Limnol. Oceanogr.*, 1, 72-84.
- Sameoto, D. D., Darrow, D. C., and Guildford, S., 1975. DDT residues in euphausiids in the upper estuary of the Gulf of St. Lawrence, J. Fish. Res. Bd. Canada, 32, 310-4.
- Schwarz, S. S., 1975. The flow of energy and matter between trophic levels (with special reference to the higher levels). In Unifying Concepts in Ecology (Eds. W. H. van Dobben and R. H. Lowe-McConnell), W. Junk, Publishers, Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands, pp. 50-60.
- Shannon, C. E. and Weaver, W., 1963. The Mathematical Theory of Communication, University of Illinois Press, Urbana.
- Sheih, Y. J. and Barber, J., 1973. Uptake of mercury by *Chlorella* and its effect on potassium regulation. *Planta*, **109**, 49–60.
- Slowey, J. F., Jeffrey, L. M., and Hood, D. W., 1967. Evidence for organic complexed copper in sea water. *Nature*, 214, 377-8.
- Sprules, W. G., 1975. Midsummer crustacean zooplankton communities in acidstressed lakes. J. Fish. Res. Bd. Canada, 32, 389-95.
- Steeman-Nielsen, E., Kamp-Nielsen, L., and Wium-Anderson, S., 1969. The effect of deleterious concentrations of copper on the photosynthesis of *Chlorella* pyrenoidosa. Physiol. Plant., 22, 1121-33.
- Stokes, P., 1975. Uptake and accumulation of copper and nickel by metal-tolerant strains of *Scenedesmus. Verh. Internat. Verein. Limnol.*, **19**, 2128-37.
- Talling, J. F., 1965. The photosynthetic activity of phytoplankton in East African lakes. Int. Rev. Ges. Hydrobiol. Hydrograph, 50, 1-32.
- Tsay, S.-F., Lee, J.-M., and Lynd, J. Q., 1976. The interactions of Cu⁺⁺ and CN⁻ with araquat phytotoxicity to a *Chlorella*. Weed Sci., 18, 596-8.
- Venkataraman, G. S. and Rajyalakshmi, B., 1971. Tolerance of blue-green algae to pesticides. Cur. Sci. (Bangalore), 6, 143-4.
- Voight, R. A. and Lynch, D. L., 1974. Effects of 2,4-D and DMSO on procaryotic and eucaryotic cells. Bull. Environ. Contam. Toxicol., 12, 400-5.
- Volterra, V., 1926. Variations and fluctuations in the number of individual species of animal communities (in Italian). Mem. A cad. Lincei, Ser. 6, 2, 31-113.
- Walsh, G. E., 1972. Effects of herbicides on photosynthesis and growth of marine unicellular algae. *Hyacinth Cont. J.*, **10**, 45-8.
- Walsh, G. E., 1975. Utilization of energy by primary producers in four ponds in northwestern Florida. In Proceedings: Biostimulation and Nutrient Assessment

Workshop, pp. 249-74, U.S. Environmental Protection Agency, Ecological Research Series, EPA-660/3-75-034, iv, 319 pp.

- Walsh, G. E. and Grow, T. E., 1971. Depression of carbohydrate in marine algae by urea herbicides. *Weed Sci.*, 19, 568-70.
- Whitacre, D. M., Roan, C. C., and Ware, G. W., 1972. Pesticides and aquatic microorganisms. Search, 3, 150-7.
- Whitton, B. A., 1970. Toxicity of heavy metals to freshwater algae: A review. *Phykos*, 9, 116-25.
- Yentsch, C. S., 1974. Some aspects of the environmental physiology of marine phytoplankton: a second look. *Oceanogr. Mar. Biol. Ann. Rev.*, 12, 41-75.
- Zarnowski, J., 1972. The effect of ethylenediamine-tetraacetic acid on the growth of *Chlorella pyrenoidosa* and its role in the dynamics of metabolism and accessibility of iron and calcium. *Acta Hydrobiol.*, 14, 353–73.
- Zingmark, R. G. and Miller, T. G., 1975. The effects of mercury on the photosynthesis and growth of estuarine and oceanic phytoplankton. *Belle W. Baruch Libr. Mar. Sci.*, 3, 45–57.