REGIONAL COPPER-NICKEL STUDY

THE TOXICITY OF HEAVY METALS, BENEFICIATION REAGENTS AND HYDROGEN ION TO AQUATIC ORGANISMS

Minnesota Environmental Quality Board

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INTRODUCTION TO THE REGIONAL COPPER-NICKEL STUDY

The Regional Copper-Nickel Environmental Impact Study is a comprehensive examination of the potential cumulative environmental, social, and economic impacts of copper-nickel mineral development in northeastern Minnesota. This study is being conducted for the Minnesota Legislature and state Executive Branch agencies, under the direction of the Minnesota Environmental Quality Board (MEQB) and with the funding, review, and concurrence of the Legislative Commission on Minnesota Resources.

A region along the surface contact of the Duluth Complex in St. Louis and Lake counties in northeastern Minnesota contains a major domestic resource of copper-nickel sulfide mineralization. This region has been explored by several mineral resource development companies for more than twenty years, and recently two firms, AMAX and International Nickel Company, have considered commercial operations. These exploration and mine planning activities indicate the potential establishment of a new mining and processing industry in Minnesota. In addition, these activities indicate the need for a comprehensive environmental, social, and economic analysis by the state in order to consider the cumulative regional implications of this new industry and to provide adequate information for future state policy review and development. In January, 1976, the MEQB organized and initiated the Regional Copper-Nickel Study.

The major objectives of the Regional Copper-Nickel Study are: 1) to characterize the region in its pre-copper-nickel development state; 2) to identify and describe the probable technologies which may be used to exploit the mineral resource and to convert it into salable commodities; 3) to identify and assess the impacts of primary copper-nickel development and secondary regional growth; 4) to conceptualize alternative degrees of regional copper-nickel development; and 5) to assess the cumulative environmental, social, and economic impacts of such hypothetical developments. The Regional Study is a scientific information gathering and analysis effort and will not present subjective social judgements on whether, where, when, or how copper-nickel development should or should not proceed. In addition, the Study will not make or propose state policy pertaining to copper-nickel development.

The Minnesota Environmental Quality Board is a state agency responsible for the implementation of the Minnesota Environmental Policy Act and promotes cooperation between state agencies on environmental matters. The Regional Copper-Nickel Study is an ad hoc effort of the MEQB and future regulatory and site specific environmental impact studies will most likely be the responsibility of the Minnesota Department of Natural Resources and the Minnesota Pollution Control Agency.

INTRODUCTION

One of the major tasks of the Regional Copper-Nickel Study is to determine the possible effects of potential copper-nickel development on the aquatic environment. This report is a summary of publications and manuscripts in preparation which deal with the toxicity to freshwater organisms of potential water pollutants from the mining, beneficiation and smelting of copper-nickel ores. The effects of nine metals, ten ore-beneficiation reagents, and hydrogen ion have been reviewed. The metals are copper, nickel, zinc, cadmium, cobalt, lead, arsenic, silver and manganese; the beneficiation reagents are sodium ethyl xanthate, potassium ethyl xanthate, sodium isopropyl xanthate, potassium isopropyl xanthate, sodium isobutyl xanthate, potassium amyl xanthate, dosium secbutyl xanthate, potassium sec-butyl xanthate, potassium hexyl xanthate and methyl isobutyl carbinol. Both experimental and case studies data are reported.

Toxicity information published between 1960 and 1976 has been emphasized in this report. Much of the information published before 1960 is difficult to interpret or has been superseded by more recent research. Several pertinent pre-1960 studies have been cited, however, as have several 1977 publications and manuscripts. The report has been organized to illustrate the relative sensitivity of different species to each pollutant, and the factors which modify the effects of these pollutants on aquatic life.

MODE OF TOXIC ACTION OF METALS AND HYDROGEN ION

Since the chemistry of receiving water determines the speciation of toxic metals, and since receiving water chemistry has also been shown to affect the toxicity of metals to aquatic life (see pages 19 to 33), it is possible to conclude that not all species of a given metal possess the same toxicity. Information on the relationship of metal speciation to chronic metal toxicity

is lacking. Data from acute toxicity experiments indicate that cupric ion is the copper species most toxic to fish (Pagenkopf et al. 1974, Andrew 1976, Chapman and McCrady 1977). The same results might be expected for other toxic metals which speciate similarly in aqueous solution.

Studies of the mechanism of toxic action of copper, nickel, zinc, cadmium, cobalt, lead and manganese have shown that lethal concentrations of these metals damage the gills of freshwater fish and cause death by suffocation (Schweiger 1957, Haider 1964, Skidmore 1970, Skidmore and Tovell 1972). In fish, sublethal concentrations of toxic metals can affect enzyme and hormone levels and other biochemical parameters (Jackim et al. 1970, McKim et al. 1970, Christenson 1972, 1975, Donaldson and Dye 1975, Larsson 1975), as well as blood volume, blood electrolyte concentrations, hematocrit and serum osmolality (Lewis and Lewis 1971, Courtois and Meyerhoff 1975, Larsson 1975, McCarty and Houston 1976). Matthiessen and Brafield (1973) found damage to the gill epithelia of sticklebacks exposed to sublethal zinc concentrations for up to thirty days. Although cause-effect relationships are difficult to determine, some of the biochemical and physiological changes enumerated above are no doubt related to detrimental long-term effects on survival, growth, and reproduction.

Several investigators have observed low blood pH (Lloyd and Jordan 1964, Packer and Dunson 1970; 1972), sodium loss (Packer and Dunson 1970; 1972), and diminished oxygen consumption (Packer and Dunson 1972) in trout exposed to lethal acid solutions. Seven-day exposures to sublethal pH levels damaged the gill epithelium and caused hypertrophy of gill mucous cells and excessive mucus secretion in brook trout (Daye and Garside 1977).

DETRIMENTAL EFFECTS OF METALS, BENEFICIATION REAGENTS, AND HYDROGEN ION

This section concentrates on the reported effects of toxic agents on animal species, the most complete and easily interpretable data. The animal data are presented in tabular form (Tables 1-37). In addition, brief, general reviews are presented of studies on bacteria and algae. While some experimental studies of effects on macrophytes are available (e.g. Hutchinson and Czyrska 1975, Walbridge 1977), the literature is quite limited and this group is not discussed. Only toxicity information pertaining to families of fishes and to orders of crustaceans and aquatic insects represented in the Study Area has been included. Geographic distribution of bacteria, algae, freshwater molluscs, rotifers, and protozoans was not considered, since little information about these groups exists in the aquatic toxicology literature.

An attempt was made to be selective in reporting toxicity information in this section. Only those pollutant effects which are obviously detrimental to the health and integrity of individuals or populations were considered. When chronic toxicity data are available for a given toxicant and species, acute toxicity data are not presented. Acute toxicity data which illustrate the relationships of water characteristics to pollutant toxicity, the effects of toxicant mixtures and adaptation to toxicants will be discussed in pages 34-36, and 39-42, respectively.

Interpretation of Tables--Concentrations listed in the tables reference in this section were measured using standard (at the time of publication) analytical methods and unfiltered test water samples unless otherwise noted. When samples were not analyzed, the calculated, or nominal concentration is given. Concentrations of metal salts are expressed in terms of the toxic metal, not the salt.

For each test species, three descriptors are listed: the common name, the scientific name if it is given by the original author or can be determined from the common name, and the life history phase at the time the effects were observed, if given.

The effect observed at the listed concentration is described along with information to aid in its interpretation. A significant effect is one which has been verified using a multiple-range test of differences between treatments and controls at an error rate of 0.05. The application factor, if given in the original publication, is reported. It lies within a range defined by the smallest fraction of the 4-day LC50 at which a significant effect was observed and the largest fraction of the 4-day LC50 at which no significant effects were observed.

If test solutions were not continuously renewed, the frequency of renewal is noted. Addition of food can affect the toxicity of unrenewed solutions of metals (Wurtz 1962, Biesinger and Christenson 1972); therefore, in bioassays of metals where solutions were not renewed, it is noted whether or not the test animals were fed.

Listed in the next four columns are those test water characteristics which greatly affect the toxicity of metals (see pages 19-33) and thus enter into the interpretation of bioassay results. Increasing pH, hardness, and alkalinity reduce the effects of toxic metals, and increasing temperature shortens the time required for most of the toxic metals to act. If a measurement of a certain parameter is not available in the original publication, "NA" is entered in the appropriate space. The tables dealing with hydrogen ion toxicity contain a column for listing the pH to which the test animals were acclimated before the bioassay began, which is usually the same as the pH of the controls in the bioassay.

Effects of Copper

Bacteria--Copper may have a stimulatory effect on growth and bacterial activity at low concentrations, while at higher concentrations toxic effects are observed. Various physiological parameters are affected differentially. Growth of Nitrosomonas europea, measured as nitrite production, was stimulated by concentrations of 0.005 and 0.06 µg/l and reduced to control levels at 0.48 µg/l (Loveless and Painter 1968). The viability of mixed cultures from natural freshwater was reduced by the addition of 1.0 µg/l $CuCl_2$. Heterotrophic activity of these cultures was reduced as concentration of 10 µg/l (Albright et al. 1972).

Algae--Copper in trace amounts is essential to the growth of algae, while at higher concentrations, toxic effects occur (Patrick 1977).

Several investigators have found copper to be toxic at low concentrations. For example, while Steemann Nielsen and Laursen (1976) observed enhanced algal growth in a lake to which copper had been added to a concentration of 25 µg/l Cu^{++}, the same concentration inhibited growth in three other lakes. Goldman (1972) observed severe inhibition of photosynthesis in Clear Lake, California, at a concentration of 79 µg/l Cu^{++}, a level corresponding to only 1.25 times the normal concentration. 110 µg/l virtually stopped algal growth in this lake.

Different species respond differently to the same copper concentrations in the same test waters (Hutchinson 1973, Hutchinson and Stokes 1975). Toxic effects of copper on Chlorella vulgaris, Scenedesmus acuminata, and Haematococcus capensis were observed at concentrations of greater than 50 µg/l. Chlorella vulgaris was the most sensitive of the three species, being completely eliminated at 100 µg/l. Chlamydomonas engolmetos was unaffected at levels up to 100 µg/l but declined rapidly at higher concentrations. While effects on S. acuminata

were evident at 50 µg/l, this species apparently survived at levels up to 500 µg/l (Hutchinson 1973, Hutchinson and Stokes 1975). Strains of Scenedesmus and Chlorella isolated from lakes polluted with copper and nickel showed greater tolerance to copper than laboratory strains (Stokes et al. 1973).

Nitrogen fixation by the blue-green algae Anabaena and Aphanizomenon was adversely affected at concentrations of 5 to 10 µg/l. As a group, the blue-green algae appear to be especially sensitive to low copper concentrations (Horne and Goldman 1974, Steemann-Nielsen and Laursen 1976). However, Maloney and Palmer (1956) found six species of diatoms tested to be more sensitive than seventeen species of blue-green algae. Green algae (seventeen species) were the least sensitive.

Other toxic effects have been observed such as inhibition of silica uptake by diatoms (Goering et al. 1977), inhibition of NO_3 uptake, inhibition of photosynthetic carbon assimilation, decreased chlorophyll content, and loss of motility and cell disruption (Harrison et al. 1977, Steemann-Nielsen and Kamp-Nielsen 1970, Morel and Morel 1977, Morel et al. 1977).

The common usage of copper as an algicide has contributed to our knowledge of the toxicity of this element. Recommended levels for control of various species have been listed (Anonymous 1954).

Algal Population and Community Effects--Changes in species composition of communities are the most obvious results of exposure to copper. Species-specific sensitivity to copper is the basic cause underlying these changes. As noted above, it appears that among the algae, blue-greens are most sensitive to copper. Horne and Goldman (1974) found that 5 µg/l Cu decreased nitrogen fixation by 90 to 95 percent in 2 days while photosynthesis was unaffected.

Green algae (mostly Oocystis) and diatoms (Melosira) were favored as blue-greens (Aphanizomenon and Anebaena) were inhibited. The authors suggested that an inflow of water with a high copper content may have been the cause of inhibition of blue-green blooms in Onondaga Lake, New York.

Reactions to copper exposure may be more complex. Fielding and Russell (1976) observed different responses at different levels of copper in cultures containing more than one species of marine algae. At low concentrations species composition changes were the result of changes in competitive relationships, probably caused by differential sensitivity of the algal species. At higher concentrations annidation occurred, the growth of one species being stimulated above unialgal levels by the presence of the other species. Enhancement of growth at the higher concentrations could be the result of removal of copper by complexation with extracellular products of algal metabolism or by absorption on living or dead cells.

Decreased diversity of algal communities and altered dominance relationships occurred within a week of exposure to copper in enclosures in a marine environment. Centric diatoms and dinoflagellates decreased in abundance while pennate diatoms and microflagellates increased (Thomas and Siebert 1977). Copper-tolerant assemblages have developed, tolerance being related to the initial exposure concentration (Harrison et.al. 1977). Algal bioamass was observed to increase, which may have been the result of the resurgence of resistant species, or decreased predation by more sensitive zooplankters (Thomas et al. 1977).

Rotifers and Protozoans--Published data on the toxicity of copper to freshwater rotifers and protozoans are summarized in Table 1. Acute effects were observed at copper levels between 700 and 1100 µg/l.

Crustaceans--Information on the toxicity of copper to freshwater crustaceans is presented in Table 2. Cladocerans, amphipods and crayfish were affected by copper levels less than 100 µg/l. Two copepod species and one isopod species were killed at copper concentrations between 500 and 2500 µg/l.

Molluscs--Table 3 summaries information on the toxicity of copper to freshwater molluscs. Copper was acutely toxic to snails, the only group studied, at levels between 13 and 69 µg Cu/l.

Aquatic Insects--Results of tests of the toxicity of copper to aquatic insects are presented in Table 4. Various species differ widely in sensitivity. Toxic concentrations ranged from 14 to 3200 µg/l copper. In general, mayflies were the most sensitive group, stoneflies were more tolerant, and caddisflies were the most tolerant group. The midge Tanytarsus dissimilis was the most sensitive insect species but may not be representative of other dipterans since chironomids have been shown to be extremely resistant to metals in field situations (see pages 53-63).

Fishes--Test of the toxicity of copper to freshwater fishes are summarized in Table 5. Chronic effects on several species have been observed at copper concentrations less than 50 µg/l.

Effects of Nickel

Bacteria--At low concentrations nickel may stimulate bacterial growth, while toxic effects are observed at higher concentrations. Species differences in resistance have been observed. Various physiological functions are affected differently, and selective reversal of toxic effects by magnesium suggests that more than one mode of toxic action may be involved.

Increased counts of viable bacteria from natural freshwater resulted upon exposure to 1 µg/l Ni, while a concentration of 10 µg Ni/l caused a decrease

in cell numbers and reduced heterotrophic activity (Albright et al. 1972).

Nickel concentration of 0.5 µg/l decreased growth and acid production in Vibrio cholerae and V. elter and glucose utilization by V. elter. 1.0 µg Ni/l reduced glucose utilization in V. cholerae. Magnesium ion reversed the effects on growth and glucose utilization but effects on acid production were still evident (Lalithamma et al. 1976).

Algae--Nickel is not known to be important in the metabolism of algae. However, enhancement of growth of Chlorella vulgaris by low concentration of nickel has been observed. Optimal growth occurred at 3 µg/l. Higher concentrations inhibited growth (Fisher 1975). Of four algal species tested by Hutchinson (1973) Scenedesmus acuminuta was the most sensitive, being largely killed at 100 µg/l. The other three species grew at concentrations up to 300 µg/l, although growth of Chlorella vulgaris and Haematococcus capensis was somewhat reduced. Strains of Chlorella and Scenedesmus isolated from lakes polluted with copper and nickel showed greater resistance to nickel than laboratory strains (Stokes et al. 1973).

Algal Population and Community Effects--In a series of experiments with nickel, using natural periphyton communities growing in greenhouse streams, Patrick et al. (1975) found effects on species composition and community structure at much lower concentrations than those shown to be effective by tests with single species of algae in the laboratory. Significant reductions of diatom diversity and a shift in algal populations to blue-greens were observed at concentrations of 4 to 9 µg/l. These trends were confirmed at higher concentrations. The authors concluded that nickel is deleterious to the growth of diatoms at very low concentrations. Blue-greens were the most tolerant forms, while greens occupy an intermediate position.

Crustaceans and Rotifers--A summary of information on the toxicity of nickel to freshwater crustaceans and rotifers is given in Table 6. Toxic effects have been observed over a wide range of concentrations (95-1500 µg Ni/l). Cladocerans are generally the most sensitive organisms while copepods and rotifers are less sensitive.

Aquatic Insects--Data on the toxicity of nickel to aquatic insects are presented in Table 7. Toxic effects of nickel have been observed to occur at concentrations of 130 to 64,000 µg Ni/l. As with copper, caddisflies are the most tolerant group, stoneflies are more sensitive, and mayflies are the most sensitive aquatic insect group. The midge Tanytarsus dissimilis was the most sensitive insect but is probably not representative of dipterans as a group since other members, notably chironomids, are often among the most tolerant insects.

Fishes--Table 8 presents data on the toxicity of nickel to freshwater fishes. Chronic effects on fathead minnows (pimephales promelas) were recorded at 730 µg/l Ni while acute effects on this species and others occurred at levels greater than 4500 µg/l Ni.

Effects of Zinc

Bacteria--Albright et al. (1972) found that zinc had a stimulatory effect on growth of mixed cultures from natural freshwater at concentrations up to 1000 µg/l. However, although the viable count increased at 100 µg/l, heterotrophic activity was reduced at this concentration.

Algae--Zinc is a micronutrient necessary for the growth of algae (Walker 1953, Whitton 1970) but has been shown to inhibit algal growth at higher concentrations. Bringmann and Kuhn (1959a;b, cited in Cairns et al. 1972) exposed Scenedesmus to various concentrations of zinc for four days and

observed median threshold responses at 1000 to 1400 µg/l zinc. Patrick (1965) found a 50 percent reduction in the division rate of Navicula seminulum var. hustedtii and Nitzschia linearis when they were exposed to concentrations between 1300 and 4500 µg/l zinc for five days. The effective concentration varied with the temperature and hardness of the experimental water, being lower at higher temperatures and in soft water.

Algal Population and Community Effects--Williams and Mount (1965) exposed periphyton communities in outdoor canals to four concentrations of zinc (nominally, 0, 1000, 3000, and 9000 µg/l) for 14 weeks. A decrease in algal diversity and in the average number of dominant species with increasing zinc concentration was observed. Cladophora was found only in the control system. Communities exposed to the lowest concentration were producer dominated, with many green algae and diatoms present, whereas communities exposed to the two higher concentrations appeared to be specialized for the digestion of organic material, being dominated by fungal hyphae and bacteria. Fungal mat formation occurred at the highest concentration. The authors pointed out that this restructuring may be an artifact, as phytoplankton were continuously brought into the system and killed. Presumably, a community dominated by blue-green algae would have developed at the higher concentrations under more normal circumstances.

Rotifers and Protozoans--Few data are available concerning the effect of zinc on freshwater rotifers and protozoa (Table 9). Effects have been observed at zinc concentrations greater than 1000 µg/l.

Crustaceans--Information on the toxicity of zinc to freshwater crustaceans is presented in Table 10. Cladocerans are apparently more sensitive to zinc than copepods. Zinc is acutely toxic to copepods at levels greater than 500

µg/l while acute effects on cladocerans have been observed at levels as low as 40 µg/l.

Molluscs--Table 11 presents data on the toxicity of zinc to freshwater molluscs. Acute effects have been observed at levels between 434 and 3160 µg/l . It should be noted that the high and low value were for the same species of snail Physa heterostropha, under different test conditions.

Aquatic Insects-- Information on the toxicity of zinc to aquatic insects is presented in Table 12. The order of sensitivity among insect groups evident with respect to copper and nickel is not as apparent for zinc. Toxic zinc concentrations range from 9200 to 32000 µg/l. A mayfly was the most sensitive species, and a caddisfly and stonefly were least sensitive.

Fishes--Table 13 summarizes zinc toxicity data for freshwater fishes. Under a variety of test conditions, a wide range of toxic levels was reported (145-4600 µg Zn/l).

Effects of Cadmium

Bacteria--Cadmium reduces viability and inhibits heterotrophic activity of bacteria. Resistant populations of marine bacteria have been observed. Cultures from natural freshwater showed a reduction in cell counts when exposed to cadmium at concentrations ranging from 1 to 1000 µg/l, but were probably not significantly different from controls at 1 and 10 µg/l. Bacterial heterotrophic activity was reduced at 100 µg/l (Albright et al. 1972). Glucose oxidation in marine cultures were inhibited at 10 and 100 µg/l Cd. Greater inhibition was observed at the higher concentration. Resistant populations were observed in areas polluted by cadmium and other metals (Mills and Colwell 1977).

Algae--Information on the toxicity of cadmium to algae is quite limited.

Scenedesmus was tested in the water from which it was collected and the threshold concentration of cadmium was found to be 100 µg/l (Bringmann and Kuhn 1959a,b, cited in Cairns et al. 1972). Hutchinson (1973) studied the effects of cadmium on three species of algae. Of these, Chlorella vulgaris was the most sensitive, showing a marked decline in growth at concentrations greater than 50 µg/l. Chlamydomonas eugametos was the most tolerant and grew reasonably well even at 200 µg/l. No threshold concentration was observed. Scenedesmus acuminates was intermediate between the two, showing a gradual decline up to 100 µg/l and a more rapid decline at higher concentrations.

Crustaceans and Rotifers--Table 14 summarizes data on the toxicity of cadmium to freshwater crustaceans and rotifers. Cladocerans are the most sensitive group with acute and chronic toxic effects occurring at levels below 100 µg Cd/l. Rotifers were sensitive at 300 µg Cd/l while copepods were affected in acute toxicity tests at cadmium levels greater than 500 µg/l.

Aquatic Insects--The toxicity of cadmium to aquatic insects is presented in Table 15. As a group, insects were not found to be sensitive to cadmium. The lowest level at which toxic effects were observed was 2000 µg Cd/l, in one acute toxicity bioassay with the mayfly Ephemehella subvaria. Toxic effects on other insects were observed at levels exceeding 10,000 µg Cd/l.

Fishes--Fishes are much more sensitive to cadmium than aquatic insects (Table 16). Most species tested are affected in chronic tests at cadmium concentrations less than 100 µg/l. Brook trout (Salvelinus fontinalis) and brown trout (Salmo trutta) were affected by cadmium concentrations of less than 10 µg/l.

Effects of Lead

Bacteria--Lead does not seem to have severe deleterious effects on bacterial growth except at rather high concentrations, although impairment of certain

physiological functions has been observed. Bacteria can alter the chemical form of lead to a form which may have secondary algicidal effects. Resistant populations of marine bacteria have been observed.

Lead salts ($PbCl_2$) reduced the heterotrophic activity of mixed cultures from natural freshwater at 100 µg/l. However, an increase in counts of viable bacteria was noted at that concentration. Decreases in counts of viable bacteria occurred at 1000 µg/l (Albright et al. 1972). Tornabene and Edwards (1972) found that lead in various forms at concentrations approaching solubility limits had no effects on viability or growth of Micrococcus luteus or Azotobacter spp. Glucose oxidation by marine cultures was inhibited by lead at both 10 and 100 µg/l, the inhibition being greater at the higher concentration. Further, inhibition was less in cultures taken from areas exposed to metal effluents than in those from unpolluted areas, indicating the presence of metal-resistant microbial populations (Mills and Colwell 1977).

On physico-chemical grounds one would predict that the lead ion would not be methylated, as methyl lead is unstable in water and the methyl group would not be transferred to thelead ion (Wood 1973). However, Wong et al. (1975) have shown that methylation of Me_3Pb salts to Me_4Pb does occur in lake water or nutrient medium, and that conversion of inorganic lead salts to Me_4Pb can occur in certain sediments. Several bacterial genera have been implicated in these transformations. Tetramethyl lead is volatile and extremely toxic to algae (Scenedesmus quadricula) in exposures of short duration.

Algae--Lead is not essential in the metabolism of algae and is toxic only at high concentrations.

Reports on toxicity of lead to algae are scarce. Bringmann and Kuhn (1959a,b) reported threshold concentrations of lead to be 2500 µg/l for Scenedesmus

and 25000 µg/l for Microregma. These tests lasted four days. Hutchinson (1973) investigated the effects of lead nitrate and lead acetate on Chlamydomonas engametos, Chlorella vulgaris, and Haematococcus capensis. Both salts were relatively nontoxic at concentrations up to 5 mg/l. Some inhibition of growth of Chlamydomonas and Haematococcus was observed at 100 µg/l lead nitrate, whereas Chlorella was stimulated at all concentrations tested. In general, both Chlorella and Chlamydomonas were stimulated by lead acetate while growth of Haematococcus was somewhat inhibited at concentrations of 100 µg/l and more.

In cultures consisting of two species of marine algae, the growth of the flagellate, Platymonas subcordiformis was accelerated by the presence of Phaedoactylum tricornutum (Dayton and Lewin 1975). This effect was enhanced by the addition of lead to a concentration of 1800 µg/l . This effect was enhanced by the addition of lead to a concentration of 1800 µg/l.

Crustaceans and Rotifers--The concentrations of lead which were toxic to freshwater crustaceans and rotifers are listed in Table 17. Cladocerans were affected at levels less than 1000 µg Pb/l, while effects on copepods were noted at concentrations greater than 4000 µg/l. Lead was toxic to the single rotifer species tested at 41,000 µg/l.

Aquatic Insects--Aquatic insects are relatively resistant to lead (Table 18). Except for the mayfly Ephemerella grandis, toxic effects have been observed at lead concentrations exceeding 16,000 µg/l. E. grandis was affected at 3,500 µg/l. Mayflies were, in general, the most sensitive group.

Fishes--Toxic effects of lead on fish have been reported over a wide range of concentrations (Table 19). Chronic effects occurred at concentrations

ranging from 31 to 850 µg Pb/l, considerably lower than the concentrations which affected aquatic insects. Acutely toxic effects on fish have been observed at lead concentrations exceeding 5000 µg/l.

Effects of Cobalt

Bacteria--Concentrations of 10 and 100 µg Co/l caused significant reductions in glucose oxidation by cultures taken from Chesapeake Bay water and sediment. Populations from areas exposed to metal pollution were more resistant than those not so exposed (Mills and Colwell 1977).

Algae--Cobalt, as vitamin B_{12}, has been shown to be an essential element for several diatoms including Amphora coffeaeformis, Amphora lineolata, Nitzschia frustulum, Nitzschia ovalis, Opephora spp., and Cyclotella spp. (Lewin and Lewin 1960).

Chlamydomonas eugametos was the most sensitive of three species tested by Hutchinson (1973), being eliminated at 500 µg/l. Chlorella vulgaris and Haematococcus capensis were both more resistant. Growth of both species was reduced at 500 µg/l. Shabalina (1964) reported that the growth of filamentous green algae in aquaria was inhibited by 5000 µg/l Co.

Goldman (1966) found that the addition of 5 µg/l cobalt as $CoSO_4$ was inhibiting to phytoplankton growth under natural conditions.

Crustaceans and Rotifers--Information on the toxicity of cobalt to freshwater crustaceans and rotifers is summarized in Table 20. Chronic effects on cladocerans at 12 and 21 µg Co/l have been reported while acute effects occurred at concentrations greater than 1000 µg/l. Copepods were affected at cobalt concentrations of 4000 and 15500 µg/l in acute toxicity tests.

A concentration of 59,000 µg Co/l was found to be toxic to a single species of rotifer.

Aquatic Insects--Limited data are available on the toxicity of cobalt to aquatic insects (Table 21). The species which were tested were relatively resistant to cobalt. The lowest reported toxic concentration was 1600 µg/l Co.

Fishes--The results of two toxicity bioassays of lead using carp are summarized in Table 22. A temporary reduction in growth rate occurred at 50 µg Co/l, and the 1-day LC50 of cobalt was 86 µg/l.

Effects of Silver

Bacteria--Silver at concentrations as low as 0.1 µg/l caused some decrease in viable counts of cells and reduced the heterotrophic activity of cultures from natural freshwater. 1.0 µg/l resulted in drastic reductions in viable cell counts (Albright et al. 1972).

Algae--Silver is not essential to the growth of algae and is highly toxic. Growth of Scenedesmus acuminata and Chlorella vulgaris was reduced at 10 µg/l. Cells were largely killed at 50 µg/l. Haematocuccus capensis was more resistant and showed a gradual decrease in growth at concentrations of 100 µg/l and more (Hutchinson 1973). Strains of Scenedesmus and Chlorella isolated from lakes containing elevated levels of copper and nickel tolerated higher silver concentrations than laboratory strains, although they had no prior exposure to this element; this suggests a single detoxification mechanism (Stokes et al. 1973).

Freshwater Animals--The available data on the effect of silver on freshwater animals are summarized in Table 23. Aquatic insects were affected at concentrations between 1 and 10 µg Ag/l; fish were affected at levels between

10 and 100 µg Ag/l; a single rotifer species was affected at 1700 µg Ag/l.

Effects of Arsenic

The toxicity of trivalent and pentavalent arsenic to aquatic organisms is summarized in Tables 24 and 25. Neither form of arsenic appears to have been extremely toxic to any of the organisms which were tested.

Effects of Manganese

Algae--Manganese has been found to be important for photosynthesis in many algae. It is also involved as an enzyme activator in carbohydrate breakdown. Manganese is toxic at high concentrations.

Manganese can alter algal community structure. When concentrations are low (less than 40 µg/l) blue-green algae will displace a diatom community; if the manganese content is maintained above 40 µg/l and between 40 and 400 µg/l, a diatom community will be maintained. Higher concentrations of manganese are toxic (Partick et al. 1969).

Other Aquatic Organisms--The available data on other aquatic organisms are found in Table 26. Tests on Daphnia magna indicated chronically toxic effects at 5200 and 5700 µg Mn/l and a 2-day LC50 of 9800 µg Mn/l.

Effects of Benefication Reagents

Tables 27 to 35 summarize the available data on the toxicity of ore beneficiation reagents to freshwater organisms.

Effects of Hydrogen Ion

Information on the toxicity of hydrogen ion to aquatic insects is summarized in Table 36. Acutely toxic levels of hydrogen ion range from pH 6.6 to pH 1.5

for different species. Generally, mayflies are the most sensitive insect group.

Results of several chronic toxicity chronic toxicity bioassays indicate that fish are adversely affected at pH values of 6.0 and below (Table 37).

EFFECTS OF WATER CHARACTERISTICS ON THE TOXICITY OF METALS AND HYDROGEN ION

Temperature

The rate at which a water pollutant is taken up by an aquatic animal depends at least in part on its respiration rate, which for a poikilotherm depends in turn on water temperature; therefore, it might be expected that water pollutants exert toxic effects more rapidly at higher temperatures. The ultimate toxic effects of a pollutant are determined not only by uptake rate but also by the rates of detoxification and excretion which presumably are also reltated to temperature. In addition, temperature may affect the chemical properties of a pollutant which are related to its toxicity, such as solubility and diffusion rates. Interaction of temperatue stress and toxicant stress is not considered here. Only the results of toxicant exposure at temperatures to which the test animals were acclimated is reported.

Most of the investigations cited showed that metals and hydrogen ion acted more rapidly on fish at higher temperatures. Over longer exposure periods metals and hydrogen ion tended to be more toxic at lower temperatures.

EIFAC (1976) cited unpublished results of acute copper bioassays conducted with rainbow trout at different temperatures. Mortality began later at lower temperatures, but the 6-day LC50 at 6C was one third of the 6-day LC50 determined at 15C, and the 6-day LC50 at 2C was half that at 15C. Lloyd (1960) found that mortality of rainbow trout in bioassays of zinc began sooner at higher temperatures, but that LC50s over a temperature range of

13.5C to 21.5C were similar after one day had elapsed.

In tests conducted by Pickering and Henderson (1966), the 4-day LC50 of zinc for bluegills was similar at 15C and 25C. The 4-day zinc LC50 for fathead minnows, however, was 3 times greater at 15C than at 25C.

Sprague (1969) cited his previous unpublished work in which the toxic action of zinc on Atlantic salmon was initially faster at 17C than at 11C or 5C. After two days, however, the LC50 was higher in warmer water. This effect persisted for the duration of the 14-day experiment. The 14-day LC50 at 17C was greater than twice the 14-day LC50 at 11C, and nearly 4 times the 14-day LC50 at 5C.

Hodson (1975) used a ^{65}Zn tracer to measure zinc uptake in the gills of Atlantic salmon exposed to 14mg Zn/l at three temperatures: 3C, 11C, and 19C. Salmon took up zinc in gill tissue faster at 19C than at 11C and 3C. The rate of zinc uptake increased with time at all three temperatures. Fish which died in zinc solutions at 19C had higher zinc concentrations in their gills than those killed at 11C and 3C. These experiments showed that faster zinc uptake accompanied more rapid mortality in zinc solutions at higher temperatures, but that zinc concentrations in gills were required to cause gill damage and death at higher temperatures.

Hodson and Sprague (1975) exposed Atlantic salmon to zinc at 3C, 11C, and 19C. During the first 12 hours of the experiment fish died faster at higher temperatures at a given zinc concentration. Median lethal time in a solution of 10mg Zn/l increased by a factor of 3.1 to 3.4 with a 10C drop in temperature. After six days, mortality ceased at all temperatures. LC50s by then were above the same at 3C and 11C, but the LC50 at 17C was 1.5 times the LC50 at 3C or 11C.

Kwain (1975) exposed rainbow trout embryos to low pH levels at 5C and 10C. LC50s of hydrogen ion for embryos exposed from fertilization until hatch were pH 5.52 at 5C and pH 4.75 at 10C. The author attributed the decreased acid tolerance of embryos at the lower temperature to a longer incubation period. Juvenile rainbow trout were also exposed to low pH levels at 10C and 20C. The 4-day LC50 of hydrogen ion was pH 4.12 at 10C and pH 4.32 at 20C.

Dissolved Oxygen Concentration

Low dissolved oxygen (DO) concentrations are stressing agents in themselves. It has been suggested that any reduction in DO concentration below saturation will have a deleterious effect on fish production (NAS/NAE 1973). A fish exposed to low DO concentrations must increase its ventilation rate in order to maintain a constant rate of oxygen uptake. An increased ventilation rate in toxicant solutions bring more of the toxicant into contact with the gill per unit time and thus should increase the rate of toxicant uptake.

Lloyd (1960) exposed rainbow trout to acutely toxic levels of zinc at two different DO concentrations. When fish were acclimated to test levels of DO for 18 hours before introduction of zinc, the 16-hour LC50 of zinc was the same at DO levels of 3.65 mg/l, 6.3 mg/l and 9.45 mg/l.

Lloyd (1961a) performed similar tests with copper, zinc and lead, using rainbow trout, except that toxicity tests were continued until mortality ceased. No numberical data were given, but it was reported that the LC50s of copper, zinc, and lead all decreased to a similar extent with a decrease in DO concentration. The LC50 at 50 percent of DO saturation was about 0.8 times the LC50 at saturation; at 30 percent of saturation the LC50 was about 0.6 times the LC50 at saturation. The author made no attempt to reconcile his new zinc data with the data he presneted in his previous paper.

Pickering (1968) found that the 20-day LC50 of zinc for bluegills at 1.8 mg DO/l was 0.64 times the LC50 at 5.6 mg DO/1, and the 20-day LC50 at 3.2 mg DO/1 was 0.93 times the LC50 at 5.6 mg DO/1. Weight gain of the fish in these experiments was significantly affected by DO at the 5 percent significance level, and by zinc at the 10 percent significance level. Interaction of zinc and DO was not statistically evaluated. Fish in the lowest zinc concentration, 1 mg Zn/l, grew better than controls at all DO concentrations.

Clubb et al. (1975) found that the mortality of four insect species (Holorusia spp., Ephemerella grandis, Pteronarcella badia, and Acroneuria pacifica) in 14-day exposures to a single concentration of cadmium was greater at a DO concentration of 6.2 to 7.6 mg/l than at 4.6 to 4.9 mg DO/1. Another insect (Brachycentrus americanus) was not affected by the cadmium concentration employed at either DO concentration. Cadmium uptake by E. grandis, P. badia, and B. americanus was shown to be greater at high DO concentrations. The authors cited previous studies which had shown that the oxygen consumption and thus the metabolic rates of stoneflies and mayflies increased with increasing DO concentration.

In summary, Lloyd (1971a) and Pickering (1968) agree that low DO concentrations increase fish mortality in toxic metal solutions, although Lloyd (1960) had shown that DO concentration did not affect zinc toxicity. The growth experiment by Pickering (1968) was inconclusive as to the interaction of zinc and DO. In all three studies test fish were acclimated to the test DO concentrations before toxicants were introduced. The toxicity of cadmium to insects decreased at low DO concentrations (Clubb et al. 1975), apparently because the metabolic rates of the insects decreased.

pH

A number of studies dealing with the effects of hardness, alkalinity, and organic substances on metal toxicity seem to show that metal complexes and precipitates are nontoxic or much less toxic to aquatic life than are metal ions (pages 24 - 32). Since increasing solution pH favors the formation of complexes and precipitates, it might be expected that metals are less toxic at higher pH levels. It will be seen, however, that the findings of some investigators do not support this assumption.

Sprague (1964) reported that the median survival time of Atlantic salmon in a given zinc concentration increased as pH was increased from 7.1 to 9.1. The temperature of the test water was 17C, and hardness and alkalinity were 20 and 12 mg/l as $CaCO_3$, respectively. Test solutions were aerated and were continuously renewed.

Mount (1966) found that the 4-day LC50 of zinc for the fathead minnow decreased by nearly 2/3 as Ph increased from 6 to 8. Results were the same if zinc concentration was expressed as added zinc or as measured total zinc. Mount concluded that suspended zinc was more toxic than dissolved zinc, possibly because it collected in the gills of the test fish where it could redissolve in the lower pH environment created by excretion of carbon dioxide. However, he was unable to use this mechanism to explain why zinc solutions at pH 7 were more toxic than those at pH 6, since suspended zinc was visible only at pH 8. The relationship of pH to zinc toxicity was independent of the hardness and alkalinity of the test water. Test solutions were continuously renewed but not aerated. Test temperature was 25C. Pagenkopf (1976) presented the pH-hardness-zinc toxicity relationship in graphical form, drawing primarily on Mount's data.

Tabata (1969a) concluded that zinc precipitated at high pH was not toxic to

killifish, goby or Daphnia spp. Test conditions were not described in the English abstract.

Shaw and Brown (1974) showed that an increase in pH from 6.5 to 7.5 did not significantly affect survival times of rainbow trout in copper solutions although the pH change lowered measured cupric ion concentrations by an order of magnitude. Test temperature was 10-11C and alkalinity was 100 mg/l as $CaCO_3$. Test solutions were aerated and renewed daily.

Steeman Nielsen et al. (1969) found that copper had a greater effect on the photosynthetic rate of the alga Chlorella pyrenoidosa at pH 7 to pH 8 than at pH 5. They attributed this discrepancy to competition at low pH levels between hydrogen ion and cupric ion for active sites in algal cell membranes. A similar hypothesis has been advanced to explain the ameliorating effect of hardness on metal toxicity (pages 24-32). Experiments were conducted in unrenewed media at 15C under continuous illumination. A similar relationship of pH to zinc toxicity was shown in experiments with Hormidium rivulare and zinc-resistant strains of Stigeoclonium tenue (Say and Whitton 1977, Harding and Whitton 1977).

Hardness and Alkalinity

The relationship of hardness and alkalinity to the toxicity of metals has received a great deal of attention from aquatic toxicologists. In most published studies dealing with this subject, hardness and alkalinity have been varied simultaneously; few attempts have been made to study the individual contribution of either factor to reduction of metal toxicity.

Hardness can influence the toxicity of metals through competition for active sites in the tissues of aquatic organisms between toxic cations and those of calcium and magnesium. The magnitude of effect exerted by hardness should be

proportional to the affinity of calcium and magnesium for tissue relative to the toxic ion in question (Zitko 1976). Since the bicarbonate ion is know to complex with metal ions, alkalinity, by influencing the speciation of metals in solution, might also be expected to affect metal toxicity.

In this report a discussion of simultaneous variations in hardness and alkalinity will be followed by a discussion of variations in the individual components.

Hardness and Alkalinity Varied Together--Brown (1968) determined the acute toxicity of copper to rainbow trout in waters with different levels of hardness and alkalinity, mixing various proportions of deionized water with well water which had hardness of 320 mg/l as $CaCO_3$ and an alkalinity of 200 mg/l as $CaCO_3$. The 2-day LC50 ranged from 45 µg Cu/l at 14 mg/l hardness to 500 µg Cu/l at 320 mg/l hardness. Test temperature and solution renewal rates were not specified. The pH of the undiluted water was 7.6.

The relationship of nickel, cadmium, and lead toxicity to hardness and alkalinity was also reported by Brown and appeared to be similar to that observed for copper. Only nominal concentrations of these three metals were given, however, and these may not have represented actual concentrations at high levels of alkalinity and hardness, where some precipitation was likely.

Mount (1968) exposed fathead minnows to copper for an 11-month period in a mixture of spring water and deionized water having a hardness of 198 mg/l as $CaCO_3$ and an alkalinity of 161 mg/l as $CaCO_3$. No eggs were produced at 33 µg Cu/l, but egg production at 15 µg Cu/l was similar to that of controls. Test solutions were continuously renewed, and test temperature varied seasonally from 16c to 26C. Test pH was 7.9. Mount and Stephan (1969) conducted a

similar experiment with fathead minnows in the same spring water diluted to a hardness of 31 mg/l as $CaCO_3$ and an alkalinity of 30 mg/l as $CaCO_3$. Test pH was 7.1. Egg production was completely inhibited at 18 µg Cu/l; in the soft water the 4-day LC50 was 75 µg Cu/l.

Sauter et al. (1976) exposed brook trout embryos to copper in hard and soft water at 10C, continuing both exposures until 60 days after hatch. In hard water (hardness=187mg/l as $CaCO_3$, alkalinity=178 mg/l as $CaCO_3$, pH=6.7-7.1), the growth rate was significantly less than that of controls at 8 µg Cu/l but not at 5 µg Cu/l. In soft water (hardness=38 mg/l, alkalinity=38 mg/l, pH=6.6-7.1), the growth rate was significantly reduced at 5 µg Cu/1, the lowest treatment level.

The same authors exposed channel catfish embryos to copper in similar hard and soft waters at 22C, continuing the exposures until 60 days after hatch. In the hard water, growth and survival rates were significantly less than those of controls at 19 µg Cu/l; neither parameter was significantly affected at 13 µg Cu/l. In soft water, survival rate was reduced at 18 µg Cu/1, but not at 12 µg Cu/l. Growth rate in soft water was not affected even at the highest treatment level of 24 µg Cu/l.

Lloyd (1960) used deionized water to make two dilutions of a well water which had 320 mg/l hardness and 240 mg/l alkalinity, both as $CaCO_3$. The 2-day LC50 of zinc for rainbow trout decreased from 4 mg Zn/l to 2 mg Zn/l when the well water was diluted to 50 mg/l hardness, and to 0.5 mg Zn/l at 12 mg/l hardness. Test solutions were renewed daily. Temperature was 17.5C, and pH varied from 6.6 at greatest dilution to 7.8 in the undiluted well water. The data summarized above were also reported by Lloyd and Herbert (1962) and Brown (1968).

Mount (1966) varied hardness and alkalinity in zinc toxicity tests by mixing deionized water with a spring water which had a hardness of 400 mg/l as $CaCO_3$ and an alkalinity of 300 mg/l. When hardness was increased from 50 mg/l to 200 mg/l, the 4-day LC50 for the fathead minnow increased from 13 to 32 mg Zn/l at pH 6, from 10 to 16 mg Zn/l at pH 7, and from 5 to 12 mg Zn/l at pH 8. Test solutions were continuously renewed, and the temperature was 25C.

Sinley et al. (1974) conducted chronic toxicity bioassays of zinc in hard and soft waters using rainbow trout. The hardness and alkalinity of the hard water were 333 and 238 mg/l as $CaCO_3$, respectively, and those of the soft water were 26 and 25 mg/l as $CaCO_3$, respectively. The results of the two bioassays are not truly comparable, since the hard water test was started with 2-gram juveniles and the soft water test was started with embryos. When the mortality in the hard water test is compared with the mortality after commencement of feeding in the soft water test, the lowest zinc levels at which treatment effects were observed are found to have been 640 µg Zn/l in hard water and 260 µg Zn/l in soft water. The growth rate apparently was not affected in either test, and no spawning was observed in any experimental or control aquaria. Temperatures were 16.2C in the hard water tests and 12.7C in the soft water tests. The pH of the hard water was 7.8 and that of soft water was 6.8.

Sauter et al. (1976) exposed brook trout embryos to cadmium in hard and soft water at 10C. Both exposures continued until 60 days after hatch. Hardness and alkalinity of the hard water were 188 and 177 mg/l as $CaCO_3$, respectively, and pH was 6.7-7.1. The soft water had hardness and alkalinity of 37 and 30 mg/l, respectively, and a pH of 6.5-7.2. In hard water, growth and survival rates of brook trout were significantly less than those of controls at 12 µg

Cd/l, but neither parameter was significantly affected at 7 µg Cd/l. In soft water, both effects were observed at 6 µg Cd/l, but neither at 3 µg Cd/l.

The same authors exposed channel catfish to cadmium under similar conditions. Survival and growth rates varied erratically among treatments and between treatment replicates, precluding comparison of the results of the hard water experiment with those of the soft water experiment.

Davies et al. (1976) exposed rainbow trout to lead for up to 19 months in hard and soft water. In hard water (hardness=353 mg/l as $CaCO_3$, alkalinity=243 mg/l as $CaCO_3$), 60 percent of the fish developed curved spines at 850 µg Pb/l, and 10 percent had curved spines at 380 µg Pb/l. In soft water (hardness-28 mg/l, alkalinity=26 mg/l), 44 percent of the fish exposed to 31 µg Pb/l developed curved spines and 3 percent of those at 15 µg Pb/l did so. Lead levels in the test waters were determined by flame atomic absorption spectrophotometric analysis of nonacidified samples in which suspended solids had been allowed to settle for several hours. The hard water had a pH of 7.6 to 8.3, and the pH of the soft water was 6.7 to 7.3. The authors noted that the alkalinity and pH of the hard water decreased when lead was added. 4-day LC50s in hard and soft water were 1400 and 1170 µg Pb/l, respectively.

Pickering and Henderson (1966) reported that the acute toxicity of copper, nickel, zinc, cadmium, and lead to fathead minnows and bluegill sunfish in well water which had 360 mg/l hardness as $CaCO_3$ and 300 mg/l alkalinity as $CaCO_3$ was greatly increased by diluting the water to 1/20 of its original ionic strength. The authors did not measure metal concentrations in their test solutions, and it is likely that substantial precipitation of metals

occurred in the undiluted well water and influenced the test results. Test pH was 7.5 in the soft water and 8.2 in the hard water, and the temperature was 15C. Test solutions were not renewed.

Varying Hardness and Constant Alkalinity--Tabata (1969b) performed bioassays of toxic metals in synthetic waters of 25 and 100 mg/l hardness as $CaCO_3$. Hardness was introduced by adding calcium and magnesium chlorides. The alkalinity of both types of water was 30 mg/l as $CaCO_3$. Test solutions were not renewed during experiments, and the English abstract of Tabata's paper does not state whether or not metal levels were measured. Temperature of the test water ranged from 21 to 23C, and test pH ranged from 6.8 to 7.1. The results of the experiments are shown in Table 38.

Tabata (1969c) conducted a series of 1-day bioassays of zinc in eight natural waters ranging in hardness from 14 mg/l to 200 mg/l as $CaCO_3$, using Daphnia spp. There was a strong positive correlation between LC50 and hardness which suggests that hardness was an important factor in determining zinc toxicity. Test solutions were not renewed, and it is not certain whether or not zinc levels were measured. Alkalinity values for the different waters were not reported in the English abstract.

Geckler et al. (1976) conducted three series of acute toxicity bioassays of copper in a stream water, using bluntnose minnows. Characteristics of the stream water varied among the three series. In each series, different amounts of calcium chloride and magnesium sulfate were added to the test water to increase its hardness without materially altering the alkalinity or the Ca/Mg ratio. A fourth series of bioassays was done with spring water to which $CaCl_2$ and $MgSO_4$ were added, again without altering the

Ca/Mg ratio. Test solutions in these experiments were not renewed. Temperatures varied from 22 to 26C. Table 39 summarizes the test results.

Zitko and Carson (1977) determined the acute toxicity of copper, zinc, and cadmium to Atlantic salmon in a water of constant alkalinity (unreported) to which various concentrations of calcium and magnesium chlorides were added. Survival times of fish in the zinc solutions increased with increasing concentrations of magnesium, but were not affected by calcium. Neither calcium nor magnesium affected the toxicity of copper and of cadmium.

The authors used the competition mechanism discussed above to explain their results. They proposed glycine binding constants as approximations of the relative affinities of different cations for fish tissue. The observed relationship of the toxicity of copper and zinc to calcium and magnesium levels was consistent with the predictions based on this model. However, the model indicates that magnesium will compete with cadmium for active sites in fish tissue, whereas magnesium actually had no effect on cadmium toxicity.

Harding and Whitton (1977) and Say and Whitton (1977) exposed the algae Stigeoclonium tenue and Hormidium rivulare to zinc solutions containing various concentrations of calcium and magnesium chlorides. Both calcium and magnesium reduced zinc toxicity to zinc-resistant strains of the two species. Magnesium had little effect on zinc toxicity to zinc-sensitive strains of either species, and calcium reduced the toxicity of zinc only to some of the sensitive strains of H. rivulare. Calcium also reduced the toxicity of cadmium to a zinc-resistant strain of H. rivulare.

Varying Alkalinity and Constant Hardness--Using a cupric ion selective electrode, Stiff (1971a) showed that copper-bicarbonate complexing could account for the variation in copper toxicity in hard and soft waters observed by other investigators if cupric ion were the toxic form of copper. Pagenkopf et al. (1974) incorporated water chemistry data and LC50s from six acute toxicity bioassays of copper conducted by different investigators with different waters into a chemical equilibrium model. The model was used to predict copper speciation in the test waters, taking into account hardness and complexation by both bicarbonate and hydroxide. Of the five copper species predicted by the model to have been present in lethal solutions, cupric ion varied leased in concentration from test to test, much less than total copper. In all but the softest waters, most of the copper was complexed with carbonate, according to the model's predictions. The authors concluded that cupric ion is the most toxic copper species and that alkalinity controlled cupric ion concentration to a greater extent than did any other factor in the experiments whose results were analyzed.

Andrew (1976) studied the acute toxic effects of copper on fathead minnows in Lake Superior water (hardness=45 mg/l as $CaCO_3$, alkalinity=42 mg/l as $CaCO_3$, pH=7.4-8.1) to which sodium bicarbonate had been added to increase the alkalinity. Median survival time in a solution with 159 µg Cu/l increased from 9.2 hours to 114 hours when the alkalinity was increased by 100 mg/l. Test solutions were not renewed; temperature was not specified.

Andrew et al. (1977) investigated the acute toxicity of copper to Daphnia magna in Lake Superior water with additions of sodium bicarbonate. Test temperature was 18C, and pH ranged from 7.9 to 8.1. Table 40 summarizes the test results. Increasing the alkalinity increased both the solubility of copper and the survival time of the test animals.

Summary--It has been shown repeatedly that toxic metals become less toxic to fish when the hardness and alkalinity of the dilution water are both increased. This decrease in toxicity appears to be less pronounced in tests of the chronic effects of copper and cadmium than in acute toxicity tests, but was more pronounced in chronic toxicity bioassays of lead than in the accompanying acute toxicity bioassays.

In experiments where hardness was varied and alkalinity was held constant, the toxicity of nickel, zinc, cobalt, and manganese decreased with increasing hardness. The effects of hardness on copper and cadmium toxicity were not consistent.

Increasing alkalinity without increasing hardness decreased the toxicity of copper; this relationship is likely to hold for other toxic metals as well. It would be difficult to assess the relative importance of hardness and alkalinity in influencing metal toxicity on the basis of the toxicological literature, although the work of Stiff (1971a) and Pagenkopf et al. (1974) indicates that alkalinity may be the more important factor.

Organic Substances

The ability of organic molecules to decrease the toxicity of metal solutions to aquatic animals is well recognized. Nishikawa and Tabata (1969) and Black (1974) have shown that the toxicity of a metal solution containing an organic compound is inversely related to the stability constant of the metal-organic complex which is formed.

Most surface waters contain humic substances which result from the decomposition of plant material. Humic substances can be divided into two

main fractions, humic acids and fulvic acids, which are distinguished on the basis of their solubilities at low pH (Stiff 1971b).

Carson and Carson (1972) determined the acute toxicity of copper and zinc to juvenile Atlantic salmon in the presence of humic acid. Their experimental results are shown in Table 41.

Humic acid reduced the toxicity of copper in these experiments but did not affect zinc toxicity. Hardness of the test water was 14 mg/l as $CaCO_3$. Temperature was 3.8-4.8C and pH was not reported. Test solutions were continuously renewed.

Brown et al. (1974) added different amounts of humic substances (equal proportions of peat extract and commercial humic acid) to aqueous solutions containing 2 mg Cu/l. Median survival times of rainbow trout in these solutions ranged from 470 min with no humic substances added to 1050 min with 4.5 mg added humic substances/l. Test solutions were not renewed. Test temperature was 15C, pH was 7.0, and hardness was 250 mg/l as $CaCO_3$.

Wildish et al. (1971) and Cook and Cote (1972) found that the ability of humic acid to decrease the toxicity of copper-zinc mixtures to Atlantic salmon was impaired at water hardness levels above 80 mg/l as $CaCO_3$.

Zitko et al. (1973) used a cupric ion selective electrode to measure the potential toxicity of copper solutions containing humic and fulvic acids. They predicted that fulvic acid in concentrations of 5 to 10 mg/l would be approximately twice as effective as equal concentrations of humic acid in reducing copper toxicity.

JOINT TOXICITY OF METALS

Since most polluted waters contain more than one toxic substance, the need to understand the biological effects of toxicant mixutres is apparent. Increasing efforts have been devoted in recent years to the study of mixtures of pollutants.

Terminology used to describe the joint action of toxicants in mixtures can best be defined by illustration. Let us suppose that two different solutions of equal toxicity are prepared from two different toxicants. If one toxicant is, say, twice as potent as the other, its solution would have to be half as concentrated as the solution of the other in order to have the same toxicity. The two toxicants are said to be additive in their joint effect if any mixture made up of the two equally toxic solutions is just as toxic as either of the single-toxicant solutions is by itself. A more-than-additive joint effect is indicated if the mixture is more toxic than either of the component solutions, and the joint effect is less-than-additive if the mixture is less toxic than the solutions. It should be understood that the term "less-than-additive joint effect" still implies that both components of the contribute to the toxicity of the mixture. This term is not equivalent to the term "antagonism" which signifies a reduction of the potency of one toxicant in the presence of the other. This terminology for describing joint toxicity is less precise than that proposed by Anderson (1973) and by Muska and Weber (1977), but will serve the purposes of this report.

Table 42 summarizes the results of studies dealing with mixtures of toxic metals. No studies of the effects of mixtures on freshwater animals other

than fish were found in the literature. Two publications pertaining to an exotic fish, the guppy, were cited because they report the only published work dealing with effects of copper-nickel mixtures.

The table shows that copper and nickel were additive in their joint lethal effect on the guppy. Copper-nickel mixtures manifested a more-than-additive effect on food consumption and an additive effect on food conversion efficiency of the guppy. The effect of copper-nickel mixtures on weight gain of guppies was more than additive when rations were unlimited and growth depended on appetite, and strictly additive when, because rations were restricted, growth depended on the efficiency of food conversion.

Only the lethal effects of copper-zinc mixtures have been reported in the literature (Table 42). Both additive and more-than-additive effects have been observed. It may be significant that more-than-additive effects have not been demonstrated in hard water.

The lethal effects of copper, nickel, and zinc in a mixture of the three metals were shown to be additive. The chronic effects on the fathead minnow of another mixture of three metals, copper, zinc, and cadmium, were studied by Eaton (1973). Chronic effects of the individual metals on the fathead minnow in the same dilution water had been reported earlier by other investigators. The results of Eaton's experiment do not show the extent to which addition of toxicant effects occurred, and thus are not shown in Table 42; it can only be stated that copper and zinc both appeared to contribute to the toxicity of the mixture while no toxic effects could be readily attributed to the presence of cadmium.

Hutchinson and Stokes (1975) studied the effects of copper-nickel mixtures on the growth of laboratory cultures of Chlorella vulgaris and Haematococcus capensis. Their results showed that both metals contributed to the toxicity of copper-nickel mixtures. They claimed that the joint toxicity of copper and nickel to both species was more-than-additive, although their experiments were not designed in a manner which could demonstrate this conclusively.

ATTRACTION TO AND AVOIDANCE OF TOXIC METALS

Whether or not aquatic animals are attracted to or can avoid toxic concentrations of pollutants is a matter of great importance to biologists who try to evaluate the effects of pollutants on natural populations. A number of experiments designed to test the attraction and avoidance responses of fish have been reported.

Kleerekoper et al. (1972) introduced a continuous flow of water into a large tank. Part of the influent water contained copper chloride. Goldfish placed in the tank were weakly attracted to, or trapped within, the resulting mass of copper chloride solution in which the copper concentration ranged mostly from 11 to 17 µg Cu/l. It was shown that the chloride ion was not responsible for this behavior change. The test temperature was 18 to 20C, and the pH was 8.4. The hardness of the test water was 5 mg/l as $CaCO_3$, and the alkalinity was 266 mg/l as $CaCO_3$.

Timms et al. (1972) used the same apparatus, dilution water, and copper concentrations as those used by the above-named authors in conducting experiments with goldfish, channel catfish, and largemouth bass. Goldfish

and channel catfish tended to orient themselves toward the source of copper, while the behavior of the largemouth bass did not appear to be affected by the copper gradients present in the tank.

Kleerekoper et al. (1973) studied the response of goldfish to copper gradients in a circular tank. Radially positioned partitions divided the tank into 16 sections shaped like slices of pie. Each section received water at its outside edge and was open at the opposite end, discharging water into an open area in the center of the tank, which contained a drainage standpipe. A continuous flow of copper chloride at 100 µg Cu/l was introduced into two of the sections. The other 14 sections received clean water. The copper concentration gradients were steeper in this apparatus than in the apparatus used by Kleerekoper et al. (1972) and Timms et al. (1972). In addition, one of the copper-polluted sections of the tank and one of the clean-water sections were heated to 21.4C; the rest were at 21.0C. Goldfish tended to avoid the unheated chamber containing copper, but were attracted to the heated copper-free chamber, and were attracted even more strongly to the heated chamber containing copper. Test water chemistry was similar to that described in the earlier publications cited.

Westlake et al. (1974) used the same apparatus and test water as those used by the above-named authors, but tested four different copper concentrations. Only one of the sixteen chambers received copper, and the temperature in all chambers was 21C. Goldfish tended to avoid the copper-polluted chamber with all the copper concentrations that were tested. The degree of avoidance of 10 mg Cu/l, the highest concentration, was only slightly greater than that of 5 µg Cu/l, the lowest concentration.

Carson and Carson (1973) constructed a narrow trough in which copper sulfate solutions flowed from one end and clean water flowed from the opposite end. Both solutions drained from the center, creating a sharp boundary between the copper-polluted water and the clean water. Juvenile Atlantic salmon placed in the trough tended to avoid the lowest tested copper concentration, 13 µg Cu/l, and their preference for clean water increased with increasing copper concentration. Additions of 5, 10, and 20 mg/l of humic acid to the copper solutions diminished the avoidance response in proportion to the humic acid concentration. The test temperature was 9C, and the hardness of the test water was 14 mg/l as $CaCO_3$.

Sprague (1964b) studied the behavioral responses of juvenile Atlantic salmon to copper sulfate, zinc sulfate, and copper-zinc mixtures, using the trough described above. The index of response used by Sprague was the threshold avoidance level, which he defined as the metal concentration to which half the test fish showed a statistically significant avoidance reaction. The threshold avoidance levels for copper and zinc were 4 µg/l and 56 µg/l, respectively. The effects of copper-zinc mixtures on avoidance appeared to be somewhat more than additive. The background copper concentration was 2 µg Cu/l, and 3 µg Zn/l was also present in the dilution water. Hardness and alkalinity of the test water were 15 and 12 mg/l as $CaCO_3$, respectively. The test temperature was 18C, and the pH was 7.5.

Sprague (1968) used a trough to study the behavioral response of juvenile rainbow trout to zinc sulfate in the dilution water described above. The avoidance threshold was 9 µg Zn/l. When the level of zinc in the dilution water was increased from 3 µg Zn/l to 10 µg Zn/l, the avoidance threshold increased to 14-17 µg/l. The zinc avoidance threshold determined at 17C was not significantly different from that at 10C.

A conclusion which can be drawn from all of these studies is that fish can detect metal concentrations well below lethal levels. Avoidance was shown to occur only in apparatus which created a steep metal concentration gradient. In a less confining tank in which copper concentration gradients were not as steep, a weak attraction to the copper source was observed. In the experiments conducted by Sprague (1968), the test fish appeared to react to a concentration difference rather than to an absolute level. When the background zinc level was increased, the avoidance threshold rose by an equivalent amount.

Humic acid diminished the tendency of rainbow trout to avoid copper solutions; it is likely that other water quality parameters which affect the lethality of metal solutions would influence the avoidance response as well. Although temperature change in one experiment did not affect the avoidance threshold, the responses of fish to copper solutions in another experiment changed from avoidance to attraction with an increase in temperature.

Behavioral differences among species may influence their respective avoidance reactions. Sprague (1964b, 1968) found that rainbow trout avoided lower zinc concentrations than did Atlantic salmon. He attributed the discrepancy to the tendency of the salmon to remain motionless in one part of the test trough while the rainbow trout swam more freely, thus becoming more aware of zinc concentration gradients.

ADAPTATION TO TOXIC METALS

The ability of aquatic organisms to adapt to stress has important implications for the study of the biological effects of water pollution. A

number of investigators have tried to assess the degree to which aquatic species can adapt to toxic metals and low pH levels.

Lloyd (1960) found that prior exposure to sublethal zinc concentrations increased the survival times of juvenile rainbow trout in lethal zinc solutions. Trout placed in a solution of 10 mg Zn/l without prior exposure to zinc had a median survival time of 290 min, while the median survival times of groups of trout previously exposed to 2.5 and 3.5 mg Zn/l for 14 days were 400 min and 500 min, respectively, in a 10 mg/l solution of zinc.

Sinley et al. (1974) exposed rainbow trout embryos to zinc, continuing the exposure until 20 months after hatch. Other fish from the same batch of embryos were hatched and reared in zinc-free water. The second group was marked and then placed in the zinc exposure chambers with the first group just 25 days before the zinc exposure was terminated. The group which had been exposed to zinc since before hatch had a 14 percent mortality over the entire period of exposure to 140 µg Zn/l, while the group first exposed to zinc as juveniles suffered a 59 percent mortality at the same concentration.

Spehar (1976) exposed two groups of flagfish (Jordanella floridae) to zinc. Exposure of the first group began just after fertilization; the second group was hatched in zinc-free water and its exposure to zinc began the second day after hatch. Both experiments continued to 100 days after hatch. The group exposed to zinc since before hatch suffered a 25 percent mortality at 139 µg Zn/l over the test period, while there was total mortality of the group first exposed to zinc as one-day-old sac fry.

Stokes et al. (1973) isolated the algae Scenedesmus acutiformis and Chlorella fusca from two lakes which contained high levels of copper and nickel. They determined the effects of copper and nickel on the growth of the two isolates and of laboratory cultures of the same two species. The lake isolates were more resistant to copper and nickel than were the laboratory cultures.

Harding and Whitton (1976) and Say et al. (1977) found that populations of the algae Stigeoclonium tenue and Hormidium spp. present in zinc-polluted waters were more resistant to zinc in laboratory bioassays than populations from waters containing only trace levels of zinc. The increase in resistance was shown to be a result of genetic adaptation.

Brown (1976) studied the toxicity of copper and lead to samples from five populations of the isopod Asellus meridianus. The populations were from five different polluted and unpolluted waters in a 200-year-old mining district. The populations which had been exposed to the highest concentrations of either copper or lead were the most resistant to that metal in acute and chronic toxicity tests, and were somewhat more resistant than a control population to the other metal as well. Descendents of the most lead-resistant sample were reared in clean water, yet proved to be as resistant to lead as their parents.

McIntosh and Bishop (1976) tested the acute toxicity of cadmium to bluegills from two sources. The first was a lake which had been contaminated by effluents from a brass works since 1968. The mean concentrations of cadmium, zinc, and lead in this lake were 5 µg/l, 226 µg/l, and 22 µg/l, respectively, in 1974; and 1 µg/l, 46 µg/l, and 8 µg/l, respectively, in 1975, when the

fish were collected. The other group of bluegills came from a commercial hatchery which received unpolluted water. The four-day LC50s of cadmium for the two groups were nearly identical.

Chronic toxicity experiments have been conducted in which three successive generations of brook trout were continuously exposed to cadmium, lead, and zinc (Benoit et al. 1976, Holcombe et al. 1976 and 1977). These studies did not reveal significant changes in the resistance of successive generations of brook trout to sublethal concentrations of any of the metals.

Lloyd and Jordan (1964) acclimated three groups of rainbow trout to pH levels of 6.55, 7.50, and 8.40 for 5 days, and then exposed each group to pH levels from pH 3.0 to pH 3.9. In spite of the differences in pH levels to which they had been acclimated, all three groups had similar median survival times in the acutely toxic solutions.

Falk and Dunson (1977) acclimated groups of brook trout to pH levels of 5.0 and 5.8 for 2-hour and 24-hour periods. Control groups were acclimated for periods from 1 to 2 days at pH 7.9 and 8.4. All groups were then exposed to acid solutions with pH 3.15. Acclimation to low pH did not consistently increase or decrease survival times at lethally low pH levels.

The foregoing studies have shown that exposure to elevated levels of a particular metal can increase the resistance of aquatic organisms to that metal. Acclimation to low pH levels has not been demonstrated. The resistance of algal and invertebrate populations was heritable; high metal levels over many generations had evidently selected against sensitive genotypes. The results of three-generation chronic exposure experiments with brook trout suggest that genetic differences in resistance to toxic metals may appear only after a long time.

APPLICATION OF LABORATORY TOXICITY DATA

The difficulty of applying laboratory toxicity data to natural aquatic ecosystems is well recognized, as a variety of complex problems must be considered. First, the chronic effects of pollutants on only a few species have been studied, and the relations between water chemistry and chronic toxicity must, in most cases, be assumed on the basis of results of acute toxicity bioassays. Second, laboratory experiments usually measure only the direct effects of toxicants, while toxicants in an ecosystem can affect an organism by changing its physical and chemical environment in ways that cannot be duplicated in laboratory exposure systems, or by affecting its prey, its predators or its competitors. Third, most polluted waters contain more than one toxicant, yet the effects of toxicant mixtures on many plant and animal taxa are unknown.

Experimental Studies

A number of investigators have tried to relate the results of toxicity bioassays of metals to observations on the effects of metal pollution in natural waters. Discrepancies between laboratory results and field observations were in all cases attributed to specific factors which may have influenced metal toxicity in the field but were not taken into account in the laboratory tests. The effects of organic and inorganic complexing agents which were mentioned by Grande (1967) and McIntosh and Kevern (1974) are discussed on pages 24 - 33. Avoidance of sublethal metal concentrations which was observed by Geckler et al. (1976) is discussed on pages 36-39.

Grande (1967) noted that salmonid fish were present in some lakes which contained copper levels shown to be lethal to the same species in laboratory experiments. Zinc was also present in these lakes in substantial concentrations. The author attributed the discrepancy between laboratory and field observations to the presence of nontoxic metal-organic complexes in the polluted lakes.

McIntosh and Kevern (1974) determined the 4-day LC50 of copper for the cladoceran Daphnia pulex and the copepods Cyclops spp. in the laboratory, using water from three newly-filled, artificial, outdoor ponds. The following year, each of the ponds was given a single dose of copper. Dissolved copper concentrations in relation to time are presented for only one of the ponds, along with populations of cladocerans and copepods during the same time period. As predicted on the basis of their high resistance to copper in laboratory bioassays, copepod populations were not affected by the addition of copper to the pond. Cladoceran populations in the pond were decimated by the copper addition, which was much greater than that which they could tolerate in laboratory bioassays. However, the numbers of cladocerans in the pond began to rebound while dissolved Cu levels were still 5 to 10 times as high as the lethal levels indicated by laboratory tests. The authors suggested that soluble nontoxic copper complexes were formed in the pond which were not present in the laboratory bioassay water, which had been taken from the ponds the previous year, shortly after they had been drained and refilled.

Calamari and Marchetti (1975) placed caged rainbow trout at various depths during different seasons in a lake polluted with copper and ammonia. While ammonia appeared to have little effect on the test fish, rates of death attributable to copper agreed well with published data on acute toxicity of copper to rainbow trout.

Geckler et al. (1976) found that fish in a stream experimentally polluted with copper failed to spawn in copper concentrations at which spawning occurred in tanks, using stream water. This discrepancy occurred because the fish avoided copper in the stream, but fish confined in the tanks could not do so, and

spawned in copper solutions which they apparently would have avoided if given a choice. Nevertheless, laboratory tests underestimated field effects only by a factor of 2.

Nehring and Goettl (1974) conducted toxicity bioassays of different dilutions of zinc-polluted stream water using rainbow trout. The 14-day LC50 of zinc in polluted stream water was nearly identical to the LC50 which had been previously determined by adding reagent-grade zinc to unpolluted water with similar characteristics.

Effects of Pollution by Metals and Hydrogen Ion on Natural Aquatic Communities and Comparisons of Observations from Case Studies with Predictions from Laboratory Experiments

This section deals with effects on aquatic communities that have occurred as a result of heavy metal and hydrogen ion pollution.

Cases of heavy metal pollution are presented first. The effects on different groups of organisms are presented separately. Secondary division is by metal(s) involved, although because more than one metal is usually present this division is somewhat informal. Metal levels cited are given as ranges or as maximums where possible. When necessary, more than one value is cited. Other pertinent water quality information, such as pH, hardness, etc. is given when available. Numbers in parentheses refer to the individual case studies as listed.

Field observations on the effects of low pH on aquatic organisms are then presented. Acid-stressed communities have been studied in regions receiving acid precipitation and acid mine drainage. Heavy metal pollutants are often present in these cases. Other factors such as iron precipitation, siltation, the depletion of dissolved oxygen, and decreased CO_2 and inorganic carbon have been observed where acid mine drainage occurs (Parsons 1968). These factors may complicate the interpretation of the effects of low pH on aquatic organisms.

The effects on major groups of organisms are considered separately.

Observations of the effects of metals and hydrogen ion on natural communities can be compared with varying degrees of success to the results of laboratory experiments. In addition to the problems discussed on page 43 much of the difficulty stems from the inability or negligent failure of field observers to record spatial and temporal variations in toxicant levels and water chemistry parameters, if these parameters were measured at all. In some instance, particularly in older case studies, certain toxic constituents may have been measured inaccurately or even ignored. Nevertheless, applicable laboratory toxicity data is compared to observations from case studies in appropriate sections.

Metals Case Studies-Algae

Decreases in abundance and numbers of species and changes in community structure have been observed to occur in response to heavy metal pollution (1-7). Algae appear to be quite sensitive to copper, and blue-greens are the least resistant group (1,2). Effects on populations have been observed at very low copper concentrations. Rather high levels of other metals may be tolerated by algae, although community structure is generally altered and standing crops are reduced. Algal mat formation has been observed in some cases (8).

Copper

1) Copper (4 lbs $CuSO_4$/acre added concentration in top 10 ft estimated at 25-35 µg/l). Lake Winnesquam, NH (Sawyer 1970).

Changes in algal community structure were observed. Blue-greens were the most sensitive group. Anabaena circinalis and Synura decreased in abundance, while Dinobryon first decreased, then became dominant. Oscillatoria increased after treatment, probably because of decreased competition and increased availability of nutrients.

2) Copper (Cu = 40-100 µg/l; pH-6.7-9.3; higher in surface waters; hardness= 69-92 mg/l). Torch Lake, Mich. (Wright et al. 1973)

Increased copper levels due to spills of copper leach liquor occurred in 1971. Samples taken in 1972 showed green algae to be dominant, whereas previously the communities were dominated by diatoms. Blooms of Anabaena were observed in 1972.

3) Copper (Cu = 100 µg/l). England (Butcher 1946, cited in EIFAC 1976).

Algal numbers were severely reduced by discharges from a copper works and effects on numbers of species and species composition could be detected 30 miles downstream from the discharge.

Toxic effects of copper on algae have generally been observed at levels between 50 and 100 µg/l in laboratory tests (see pages 5-7), although different species may vary considerably in their susceptibility. Effects on community composition and abundance have been observed at concentrations of 25-100 µg Cu/l (1, 2 and 3).

Copper-Nickel

4) Copper-Nickel (Cu to max. of 520 µg/l; Ni to max. of 6360 µg/l, see below). Lakes near Sudbury, Ontario (Whitby et al. 1976, Stokes et al. 1973).

An increase in standing crop was observed with increasing distance from smelters. The increase was negatively correlated with both copper and nickel levels. Standing crops of algae were negligible in lakes near the smelters (Baby Lake-Cu 520 µg/l, and Alice Lake-Ni 6360 µg/l). Dill Lake, located about 7 miles from the smelters, had a standing crop of 1154-3288 cells/ml. Copper, nickel, pH, and algal cell counts in 5 lakes in the Sudbury area were as follows:

LAKE	Cu	Ni	pH	#s (cells/ml)
Alice	60	6400	6.3	Neg
Baby	520	2700	4.1	Neg
Daisy	200	400	6.1	11-523
Richard	5	150	6.4	427-1496
Dill	3	---	6.7	1154-2121

Species diversity and community composition were also affected. The number of species in Baby Lake was 3, while that in the more distant Dill Lake was 50. Polluted lakes were dominated by green algae, whereas diatoms were dominant in other lakes. Tolerant strains of Chlorella and Scenedesmus were isolated from polluted lakes.

Nickel concentrations of 100 to 300 µg/l have been observed to inhibit the growth of algae. Effective levels may be much lower (see page 9). Decreases in algal standing crop and species diversity were observed in Sudbury area lakes in which copper and nickel levels ranged from 60-520 µg/l and 400-6400 µg/l, respectively. Either metal alone could have caused these effects. In Richard Lake where copper and nickel levels were only 5 and 150 µg/l, respectively, observed reductions in standing crop could have been due to nickel pollution.

Lead-Zinc

5) Lead-Zinc (Pb = 360-15,000 µg/l; Zn = 18,000-20,000 µg/l; pH = 6.0; soft water). River Rheidol, Cardiganshire (Reese 1937).

A decrease in abundance and diversity of algae was noted in this river.

While some effects on algal growth have been observed at concentration as low as 100 µg/l, algae seem to tolerate lead pollution fairly well; marked deleterions effects occur at concentrations of about 2,000 µg/l or more (see pages 14-15). Zinc does not appear to be very toxic to algae; marked responses occurring only at concentrations above 1000 µg/l (see pages 10-11). The changes in community structure and reduced diversity and abundance of algae observed in the River Rheidol (5) could easily have been caused by zinc pollution alone.

Mixtures of More than Two Metals

6. Copper, Zinc, Cadmium, Lead (Cu = not detectable to 1,800 µg/l; Zn = not detectable to 21,840 µg/l; Cd - not detectable to 480 µg/l; Pb = not detectable to 36,640 µg/l; pH = 6.4 - 7.2; Hardness = 13-37). Rivers Ystoyth and Clarach, Wales (McLean and Jones 1975).

The composition of epiphytic diatom communities were different at polluted and unpolluted sites. Hormidium spp. appeared to be the most tolerant green algae and were present in most polluted locations.

7. Copper, Zinc, Cadmiu, Lead (Cu = 3,200,000 µg/l; Zn = 2,000,000 µg/l; Cd = 19,500 µg/l; Pb = 111,000 µg/l). Silver Bow Creek, Idaho (Wood 1975)

There was a complete absence of periphyton in this heavily polluted stream.

8) Copper, Zinc, Cadmium, Lead (Cu= to max. of 570 µg/l, generally around 25 µg/l; Zn - to 300 µg/l; Cd = to max. of less than 10 µg/l; Pb = to max. of 830 µg/l; pH = 7.4-8.2; alkalinity = 135-200). New Lead Belt, Missouri (Gale et al. 1973).

Algal mat formation was observed in polluted locations. Mats consisted of Cladophor, Oscillatoria, Mougeotia, Zygnema, Spirogyra, Cymbella, etc., and included stalked and nonstalked diatoms.

In a stream polluted by sublethal levels of copper, zinc, cadmium and lead (see 8 for levels) algal mat formation occurred. Periphyton were completely absent from another stream polluted by these same metals (7). However, in this case, levels of all four metals were extremely high, and any single element could have obliterated algal populations.

Metals Case Studies-Aquatic Macrophytes

Heavy metal pollution has been shown to cause reductions in abundance and species diversity of macrophytes. Submerged plants seem to be most sensitive, and dicotyledons may be more sensitive than monocotyledons. Equisetum and Bryophytes appear to be quite resistant (1, 2, 3, 6). Laboratory studies on the toxicity of metals to macrophytes were not reviewed.

Copper-Nickel

1) Copper-Nickel (metal levels not available; see study #4, algae, for approximate levels in surface waters). Sudbury, Ontario (Gorham and Gordon 1963).

A reduction in the number of species of aquatic macrophytes with decreasing distance from the Sudbury smelters was observed. The effect was shown not to be due to changes in pH or to high SO_4 concentrations.

Copper-Zinc

2) Copper-Zinc (see below for levels). Northwest Miramichi River System, New Brunswick (Besch and Roberts-Pichette 1970).

Changes in species composition and abundance of riparian vascular plants were observed in affected areas. All species except Equisetum arvense showed some signs of damage at all affected sites. Submerged macrophytes were found to be the most sensitive group; dicotyledons were more sensitive than monocotyledons; Equisetum was the most resistant plant.

Three degrees of severity of metals pollution were described according to observed effects on macrophyte communities:

a) Low (Cu ≡ less than 1 to 34 µg/l; Zn ≡ 83 to 2000 µg/l; pH ≡ 6.5-7.2; hardness ≡ 275 - 445). Plant cover on bank gravels slightly reduced; if at all; dicots present; trees and shrubs showed no signs of damage; submerged vascular plants absent.

b) Medium to High (Cu ≡ 21.5 to 4400 µg/l; Zn≡ 220 to 16;600 µg/l; pH ≡ 6.5-7.2; hardness ≡ 350-110). Plant cover on exposed bank gravels decreased; few species present; mainly Cyperaceae; Graminae; and Equisetaceae; dicots absent.

c) Extremely High (Cu ≡ 330 to 12;100 µg/l; Zn ≡ 6;400 to 65;500 µg/l; pH ≡ 4.0-5.5; hardness = 75-430). Bank gravels barren; trees and shrubs along bank killed. Note: Values above refer to levels of surface waters; levels present in banks probably were higher.

3) Copper-Zinc (Water concentrations not available). Trondheimsfjorden; Norway (Lande 1977).

No macrophytes were present near effluents containing mining waste.

Lead-Zinc

4) Lead-Zinc (Pb ≡ 300-15;00 µg/l; Zn = 18;000-20;000; pH ≡ 6.0; soft water). River Rheidol and River Melindwr; Cardiganshire (Reese 1937).

Macrophytes were absent in several stretches of these rivers; possibly a result of siltation.

5) Lead-Zinc (Pb ≡ trace to 50 µg/l; Zn = 700-1;200 µg/l; pH ≡ 6-6.4). River Ystwyth; Cardiganshire (Jones 1940b)

Macrophytes were nearly absent.

Mixtures of More Than Two Metals

6. Copper-Zinc-Cadmium-Lead (Cu = not detectable - 1,800 µg/l; Zn = not detectable - 21,840 µg/l; Cd = not detectable 480 µg/l; Pb = not detectable - 36,640 µg/l; pH = 6.4 - 7.2; Hardness = 13-37). Rivers Ystwyth and Clarach, Wales (McLean and Jones, 1975).

Polluted areas were devoid of macrophytes other than bryophytes (Scapania undulata).

Metals Case Studies-Crustaceans

The number os studies of the effects of heavy metals on zooplankton is limited. Gammarus is more sensitive to copper and zinc pollution than planktonic crustaceans. Daphnids are more sensitive to copper pollution than copepods (1,2).

Copper

1) Copper (Cu 4 lbs Cu SO_4/acre added; concentration in top 10 ft estimated at 25-35 µg/l). Lake Winnesquam, NH (Sawyer 1970).

Daphnia abundance decreased, while Bosmina, which feeds on bacteria and detritus, became dominant. Copepods continued to constitute more or less the same proportion of the community. Changes in zooplankton communities may have been secondary effects, resulting from algal mortality. In general, these observations agree with laboratory tests, which indicate that amphipod and cladaceron species are quite sensitive to copper, with chronic effects occurring at concentrations less than 100 µg/l. Copepods and isopods have been shown to be much more resistant (Table 2).

Copper-Zinc

2) Copper-Zinc (Cu = 130 µg/l; Zn = 400 µg/l; hardness = 11 mg/l $CaCO_3$). Lake Orvsjoen, Norway (EIFAC 1976).

Gammarus lacustris was absent at these concentrations. A few planktonic crustaceans were present. Results of laboratory studies show that of the crustaceans, cladocerans are the most sensitive group to zinc, exhibiting chronic effects at levels of 158 µg/l and less. Copepods were shown to be considerably more resistant (Table 10). The amphipod Gammarus lacustris would be expected to suffer at the copper concentrations found in Lake Orusjoen. Although the source did not specify which taxa of planktonic crustaceans were present, it is likely that, at the concentrations of copper and zinc present, they were copepods.

Metals Case Studies-Macroinvertebrates-Copper

Reductions in numbers of individuals and species and decreases in diversity have resulted in areas polluted by copper. Effects are noted at concentrations well below 120 µg/l (1). At this and higher concentrations communities are dominated by chironomids (and sometimes oligochaetes), molluscs, nematodes, and amphipods increase in abundance as concentrations decrease (see also copper-zinc).

1) Copper (gradient of Cu from 120 µg/l to 23 µg/l). EPA Study, Shayler Run, Ohio (Winner et al. 1977).

The number of species present and the number of individuals present decreased as the concentration of copper increased. These two parameters were highly correlated with copper concentration. However, diversity indices were not correlated with copper concentration. Number of species was found to be most sensitive indicator of copper levels. Among the most sensitive taxa were Psephenus spp., Baetis spp., Lirceus spp. and Stenonema interpunctatum.

The community near the initial discharge was dominated by Chironomids. The community present at the lowest concentration was similar to those at control stations. Differences were found where the mean copper concentration was

38 µg/l, where low numbers of Ephemeroptera and Isopoda and an increase in numbers of Trichoptera were observed. Secondary effects may be important.

Although some midge species appear to be quite sensitive to copper (Table 4), Winner et al. (1975) found that chironomids dominated communities near the discharge in a stream artificially polluted by copper, where concentrations were approximately 120 µg/l. Effects on other groups were noted at concentrations of 38 µg/l. Only acute tests have been conducted with other species. Mayflies were the most sensitive group (Table 4). Deleterious effects of copper on snails have been observed at concentrations below 50 µg/l (Table 3).

Copper-Nickel--The effect of copper and nickel in combination has been studied in the Sudbury area.

2) Copper Nickel (Cu = 0-2,500 µg/l; Ni = 0-4,000 µg/l; pH = 3.2-7.5) Sudbury, Ontario (Johnson and Owen 1966).

A greatly impoverished benthic fauna was encountered in lakes within five miles of the Sudbury smelters and in streams receiving mine wastes. Midge larvae and tubificids were the most abundant or the only taxa at heavily polluted sites. Beetle larvae (Corixidae) were also found at some of these sites. Domestic and industrial wastes as well as high iron concentrations were contributory factors.

Chronic effects of nickel on the midge, Tanytarsus dissimilis were observed at 130 µg/l. They mayfly, Ephemerella subvaria appears to tolerate somewhat greater levels, although only acute tests were conducted using this species. Caddisflies and stoneflies appear to be the most resistant insects (Table 7). No experimental data on the toxicity of copper-nickel mixtures on macroinvertebrates are available. It appears to be safe to assume that their joint toxicity is

additive, and toxicity tests using the two metals individually suggest that the effects observed by Johnson and Owen (1966) could be accounted for by either metal.

Zinc-Decreased abundance and diversity accompaines zinc pollution (3). At levels of 200 µg/l or more, communities are dominated by insects (15). This is also true of regions of zinc-lead pollution, where molluscs, oligochaetes, crustaceans, and hirudineans are absent or rare (13). Communities in zinc-cadmium polluted streams are dominated by oligochaetes and chironomids (17,16).

3) Zinc (no levels available). Molonglo River, Australia (Weatherley and Dawson 1973).

Runoff from mining wastes caused a reduction in the number of species and the number of individuals for many kilometers downstream from slime mounds. Effects were most severe at locations closest to the source of pollution.

As a group, insects are quite resistant to zinc. On the basis of results of short-term tests, mayflies appear to be more sensitive than caddisflies or stoneflies. All of these insects were more resistant than fish. Concentrations of zinc used in the experiments with insects were above 9,000 µg/l. Molluscs (snails) are somewhat more sensitive. 4-day (LC50s ranged from 434 to 3,160 µg/l for Physa heterostropha, depending on the age of the specimens and water quality parameters (see Table 11 and 12).

Copper-Zinc--In general, similar trends are noted in areas suffering from copper and zinc pollution as from copper pollution alone. The most severely polluted areas are characterized by simple communities of only chironomids and/or oligochaetes (7,8) or Chaoborus and chironomids (5). Molluscs appear to be

extremely sensitive (6,7,8). As levels decrease, nematodes may reappear, as well as several insect orders, notably Trichoptera, Diptera, and some Ephemeroptera (7).

4) Copper-Zinc (values for two lakes will be given:

	Cu	Zn	Acidity	Hardness
Mose Lake	30 µg/l	430 µg/l	4.3 mg/l	162 mg/l
Manitouwadge Lake	23 µg/l	540 µg/l	4.0 mg/l	240 mg/l).

Ontario Lakes (German 1971).

A decline in the number of taxa and in the density of individuals in affected lakes was observed. Other lakes, though polluted, showed only small changes in these parameters.

The only taxa present in the most affected lake (Mose Lake) were Chaoborus and Chironomidae, and evidence that molluscs had been eliminated by pollution was presented. A less polluted lake (Manitouwadge) contained Cheumatopsyche, Chironomidae, Heleinae, Chaoborus, and Tubificidae. Members of the Unionidae (Lampsilis siliquoidea, Anodonta grandis) and Hexagenia were found only in control lakes.

5) Copper-Zinc (water quality data not available). Trondheimsfjorden, Norway (Lande 1977)

Reduced diversity (Margalef and Simpson indices), a 53 to 64 percent reduction in the number of species present, a 48 to 92 percent reduction in abundance, and a change in dominant species was observed at affected sites.

Mytilus edulis was either absent or showed increased mortality and decreased growth at polluted sites.

6) Copper-Zinc (Cu = 130 µg/l; Zn = 400 µg/l; hardness about 11 mg/l). Lake Orvsjoen, Norway (EIFAC 1976).

Only Chironomid larvae and planktonic crustaceans were present. Gammarus lacustris, snails, and other insects were absent.

7) Copper-Zinc (total ranges and ranges of site means were: Cu=2-23 µg/l (9.8-14.4 µg/l), at control sites=0-20 µg/l (6.6); Zn=2-184 µg/l (95.8-134.1 µg/l), at control sites=0-11 µg/l (3.3 µg/l); pH=2.95-7.45 (5.12-7.34), at control sites=7.15-7.65 (7.34); hardness=38.0-463.7 (43.7-394.9), at control sites=3.8-29.3 (13.63)). Northwest Miramichi River System, New Brunswick (Cook et al. 1971).

At control sites, Trichoptera, Ephemeroptera, Diptera, Plecoptera, Odonata, Oligochaeta, and Mollusca were abundant, while at severely polluted stations only Oligochaeta were present. There were no Odonata, Nematoda, or Mollusca at any station polluted with metals.

Proceeding downstream, increased abundance and diversity occurred, and Trichopteran and Dipteran larvae were observed. At the farthest downstream stations, Ephemeropterans began to reappear. Although some improvement was evident, neither abundance nor diversity reached control levels. The effects of metals on diversity were ameliorated by hard water at some stations.

8) Copper-Zinc (Cu=35 µg/l; Zn=150 µg/l). River Skorovasselv (EIFAC 1976).

Snails and most Ephemeroptera were absent.

No investigations of the toxicity of copper-zinc mixture on macroinvertebrates have been reported. It will be assumed that joint toxicity is additive. Tables 3, 4, 11, and 12 summarize results of toxicity bioassays on the individual metals.

Snails and most Ephemeroptera were absent from a river containing 35 µg Cu/l and 150 µg Zn/l (8). The level of copper alone could account for the absence of snails and mayflies. Similarly, in a softwater lake with 130 µg

Cu/l and 400 µg Zn/l, the absence of all benthic fauna except chironomid larvae can be explained by the high copper concentration alone (6). Zinc at that level, even the absence of other pollutants, should also have been lethal to snails.

The fauna of two polluted lakes in Ontario generally was limited to Chaoborus, Chironomidae, and Tubificidae. Evidence suggested that molluscs have been eliminated by pollution (4). The high zinc levels (430-540 µg/l) alone could explain their absence, and the copper levels (23-30 µg/l) are high enough to cause a reduction in the number of insect species present.

The maximum levels of copper (23 µg/l) and zinc (184 µg/l) in rivers in New Brunswick (7) would not appear to be sufficient to have caused the observed destruction of benthic communities. Only oligochaetes were collected at the sites. However, the low pH (to 2.9) would be expected to be lethal to many organisms and silt could have contributed to the effects observed. Improvements were noted at less polluted sites.

Lead--Communities suffering from lead pollution at levels of about 200 µg/l or more are insect dominated. No turbellarians, molluscs, oligochaetes, or hirudineans were present at these levels, and the abundance of crustaceans, dipterans, and coleopterans was reduced (10,11). Molluscs and malocostracans may suffer at much lower levels, when zinc is also present. Communities suffering from heavy pollution with lead and those affected by such pollution with copper and zinc are similar. Trichopterans, when present, are free-living species (10,9). Note: Case studies numbers 9 to 13 are probably all examples of lead and zinc pollution. However, only values reported in the original papers are given.

9) Lead (Pb=200-500 µg/l; pH=6.4). River Rheidol (Carpenter 1924).

Turbellarians, Mollusca, Oligochaeta, Hirudinea, and Trichoptera were absent from polluted stretches, and Crustacea, Diptera, and Coleoptera were less abundant than at control sites.

10) Lead (Pb=trace to 300 µg/l). River Melindar, Cardiganshire (Jones 1940a).

Most invertebrates present (76 of 88 species) were insects. In polluted stretches of the river the only taxa present were insects. Carnivorous trichopterans were present in polluted areas, whereas case-carrying trichopterans were absent or severely reduced in numbers, probably because of the lack of vegetation in these stretches. Other orders of insects were reduced in abundance and number of species. The mollusc, Ancylastrum fluviatile, which was present above the waste discharges, was absent below.

11) Lead (Pb=400-500 µg/l; pH=6.4-6.8; no zinc levels were reported). River Ystwyth, Cardiganshire (Carpenter 1925).

There were no turbellarians, molluscs, oligochaetes, hirudineans, malacostracans, or trichopterans in polluted stretches, and there were fewer Entomostracans, Dipterans, and Coleopterans than in unpolluted reaches.

Effects on insects (mayflies, caddisflies, and stoneflies) in acute toxicity bioassays occurred at levels between 3500 and 64000 µg/l (Table 18). It is likely that insects are the most resistant macroinvertebrate group. Insects were the only taxa observed in polluted stretches of the Melindar River, where lead levels varied from trace amounts to 300 µg/l. Other taxa were present in unpolluted reaches. Carnivorous trichopterans were present in polluted areas, while case-carrying trichopterans were either absent or

severely reduced in numbers (10). Lead levels in the polluted sections of the River Ystwyth ranged from 400 to 500 µg/l. No turbellarians, molluscs, oligochaetes, hirudineans, malacostracans, or trichopterans were present at these sites. The abundance of dipterans, coleopterans, and entomostracans was reduced (11). Similar results were observed in polluted regions of the River Rheidol, where lead levels ranged between 200 and 500 µg/l (9,11). It is probable that zinc was also involved as a toxic agent in these studies. In later investigations, the presence of high levels of zinc in the River Ystwyth was noted (12,13). Insect populations may be affected at lead concentrations much lower than those indicated by acute toxicity tests, but other water quality parameters and secondary effects of pollution may have been involved.

Lead-Zinc--Studies in Cardiganshire, England, have documented some of the effects of lead-zinc pollution although these data are relatively old.

12) Lead-Zinc (Pb=trace to 50 µg/l; Zn=700-1200 µg/l; pH=6-6.4). River Ystwyth, Cardiganshire (Jones 1940b).

No molluscs or malacostracans were observed, while planarians, oligochaetes, and hirudineans were rare. The fauna was composed mostly of insects; dipterans were sparse, and ephemeropterans were abundant. Some Platyhelminthes and Hydracarina were noted.

13) Lead-Zinc (An=200-700 µg/l; Pb-not detectable). River Ystwyth, Cardiganshire (Jones 1958).

The fauna of this river was still primarily composed of insects, although measurable levels of lead were no longer observed. Most abundant species were: the ephemeropterans, Rhithrogena semicolorata, Heptagenia lateralis, and Baetis rhodana; the plecopteran, Chloroperla tripunctata; and the coleopteran, Esolus parallelopipedus.

No investigations of the toxic effects of lead-zinc mixtures have been conducted, and it will be assumed that joint toxicity is additive. Lead and zinc levels in the River Ystwyth were 50 µg/l and 700-1200 µg/l, respectively (12). The fauna was composed mainly of insects, with ephemeropterans abundant; molluscs were absent. These findings are generally consistent with data derived from short-term tests on the toxicity of the individual metals. Other effects noted were the scarcity of planarians, oligochaetes, hirudineans, and dipterans.

Cobalt-Nickel--The combination of cobalt and nickel has been studied in Sweden.

14) Cobalt-Nickel (Co=10-47 µg/l; no other values were given; Ni was not consistently higher below waste discharge and there was some Zn accumulation in sediments). Ricklea River, Sweden (Sodergren 1976).

The reduction in numbers of individuals present since the commencement of operation of a diamond factory was drastic. Seasonal differences in abundance were observed. Nymphs of some mayflies and blackfly larvae were present in mosses during the summer, but the winter-growing nymphs Ephemerella macromata and Baetis rhodani and blackfly larvae were absent or reduced, owing to the higher levels of cobalt observed in winter months.

The results of acute toxicity bioassays indicate that mayflies, caddisflies, and stoneflies are quite resistant to cobalt. Toxic levels ranged from 16,000 to 32,000 µg/l (Table 21). These values are several orders of magnitude greater than those which caused reductions in abundance of insects in the Ricklea River (14). Zinc pollution may have been a contributory factor. Accumulation of zinc in the sediments was observed by the author.

Mixtures of More than Two Metals--The most sensitive groups appear to be molluscs, crustaceans, and annelids, although in some cases, oligochaetes may occur as dominants. The most tolerant groups are free-living or leptocerid trichopterans, hemipterans, odonates, and some dipterans and arachnids (15-21).

15) Copper-Zinc-Lead (Cu to 400 µg/l soluble, to 2600 µg/l particulate; Zn=1200-1600 µg/l soluble, to 2600 µg/l particulate; sediment values: Cu to 5000 µg/g; Zn to 1800 µg/g; pH=5.7-7.0). River Hayle, England (Brown 1977).

A reduction in the number of species present with increase of metal levels was observed. The fauna consisted mainly of trichopterans (mostly campodeiform), odonates, plecopterans, and dipteran larvae. There were few molluscs, oligochaetes, crustaceans, or hirudineans, although some molluscs were present at sites with high levels of metals and low pH.

16) Copper-Zinc-Arsenic (Cu site means ranged from 13-300 µg/l, max. of 9900 µg/l; Zn site means ranged from 1-54 µg/l, max. of 1900 µg/l; As mean 61 µg/l; pH=neutral; hardness soft to very hard water=to 2251 mg/l). Giant and Con Mines, Canada (Falk et al. 1973).

Diversity, based on genera, was reduced at polluted sites. Frequently no benthos were present at sites closest to sources of mine effluents. Diversity increased with distance from the point of discharge.

In some severely polluted areas, only chironomids and oligochaetes were found. At less polluted sites, clams, nematodes, snails, and amphipods were present. No Ephemeroptera were observed, although they had been present before mine operations began. Some examples are:

LOCATION	Cu (µg/l)	Zn (µg/l)	As (µg/l)	Hardness (mg/l)	EFFECT OBSERVED
Baker Creek	to 9900	34-1900	--	124-427	Invertebrates absent
Yellowknife Bay	13	1-8	61	303-933	Invertebrates reduced

17) Copper-Zinc-Cadmium (Cu=30-120 µg/l; Zn=50-8000 µg/l; Cd=0-330 µg/l; pH=6.3-7.4; hardness=8.7-101 mg/l; alkalinity=12.26-36.84 mg/l). South Esk River, Tasmania (Thorp and Lake 1973).

A general decrease in the number of species present was observed at the most severely polluted sites. The increase observed at one site could have been due to decreased predation and competition.

Groups most affected by pollution were: Crustacea, Mollusca, and Annellida. Those most tolerant were Leptocerid Trichoptera, Hemiptera, and Arachnida.

18) Copper-Zinc-Cadmium (Cu=50-100 µg/l; Zn=100-21000 µg/l; Cd=10-200 µg/l; pH=6.1-7.4). Coerd'Alene River, Idaho (Savage and Rabe 1973).

Much reduced Shannon-Weiner diversity (from more than 3 to 0.07 and less) density (from 815-1925/0.5m^2 to 0-690/0.5m^2) and number of species (from 26-32 to 0-4) were observed at affected sites. Biomass consisted mainly of Chironomidae, some other Diptera, Hydracarina and one species of Ephemeroptera, Baetis tricaudatus.

19) Cadmium-Zinc-Lead (Cd=0.3-65.8 µg/l; Zn=4-17200 µg/l; Pb=3-95 µg/l; pH=6.8-8.4; hardness=200-430 mg/l; alkalinity=160-360 mg/l). Little Center Lake, Indiana (McIntosh and Bishop 1976).

No benthic invertebrates were found in most areas of the lake. Occasionally, chironomids and odonates were observed.

20) Cadmium-Zinc-Chromium (sediment levels as ppm dry wt: Cd=4-969; Zn=139-14032; Cr=38.5-2106; pH=7.5-8.5; hardness=190-312 mg/l; alkalinity = 1.2-198 mg/l). Palestine Lake, Indiana (Yost and Atchison 1972).

Oligochaetes were found in greatest abundance at sites where metal levels were highest, probably because of lack of competition from other, less tolerant groups. Chironomids increased in abundance as metal levels declined.

21) Copper-Zinc-Cadmium-Lead (max. levels in water were: Cu = 3,200,000 µg/l; Zn = 2,000,000 µg/l; Cd = 19,500 µg/l; Pb = 111,000 µg/l). Silver Bow Creek, Idaho (Wood 1975).

No benthic animals were observed in this stream.

It is difficult to evaluate the joint effects of mixtures of more than two metals on macroinvertebrates because of the lack of experimental work on the toxicity of metal mixtures and the fact that where levels for several metals have been measured in the field, the effects observed could have resulted from a single pollutant (15-21), and Tables 3, 4, 11, 12, 15, and 18).

Metals Case Studies-Fishes

Few comprehensive fish polutation surveys in water polluted by heavy metals have been undertaken. In general, the scope of these studies has been limited to certain species.

Copper--Only two field surveys have been conducted in areas polluted exclusively by copper. In most cases copper is in combination with other metals.

1) Copper (Cu = 143-354 µg/l, normal levels are less than 10 µg/l; near the mine the average Cu level is 17,509 µg/l; pH > 6.5-7.5; hardness = 70-120; high sedimentation). Panther Creek, Idaho (Platts 1972)

Trout production has been eliminated or severely reduced for a distance of thirty miles from the mine. Anadromous salmon runs have also ceased. These effects are probably a result of avoidance behavior and effects on fish food organisms, notably mayflies. Iron precipitates smothered much of the bottom flora and fauna.

2) Copper (Cu: no values were given; pH 5.5). Hiwassee River System, Tennessee (Hitch and Etnier 1974).

A mining and industrial waste discharge has altered fish populations in

several parts of the system. Notably, the main channel of the Ocoee River was completely devoid of fish and no large catostomids, petromyzontids, cyprinids, or walleyes were present, these species having been unable to repopulate affected tributaries. Only catfish are present in Sylco Creek, carp and catostomids having disappeared.

Copper has been shown to exert significant detrimental effects on trout, minnows, catfish, suckers, and bluegills in concentrations below 50 µg/l in soft and hard water. Northern pike were affected at 104 µg/l in soft water (Table 3). These values are well below those reported in Panther Creek (Platts 1972) where trout production was reduced or eliminated.

Copper-Nickel--The most significant study of copper and nickel in combination was made in the Sudbury Area.

3) Copper-Nickel (Cu = 3-520 µg/l; Ni = not detectible to 6400 µg/l; pH 4.1-7.1). Sudbury area lakes, Ontario (Whitby et al. 1976)

Fish were absent in the most heavily polluted softwater lakes. At levels of 520 µg/l Cu and 6400 µg/l Ni either toxicant could have been responsible since acute effects of nickel have been reported at levels of 5000 µg N/l (Table 8), below the 6400 µg/l Ni reported (3). Further the copper level of 520 µg/l is above the levels reported to have chronic effects on fish (Table 3).

At lower levels of copper and nickel the joint effect of the two might become significant as they are additive to more than additive for fish (Table 42).

Copper-Zinc--Where copper and zinc pollution occurred simultaneously, effects on abundance of fish have been observed at low levels of both metlas (approx. 10 µg Cu/l and approx. 100 µg Zn/l) when the pH was low (6), but not when

the pH was circumneutral (7). However, even with low copper levels found in the latter study, a decrease in populations of white sucker, walleye, and lake whitefish was observed when zinc values increased to 300 µg/l (7). Similarly, trout and salmon have disappeared from streams with zinc levels of 135 µg/l when copper concentrations were higher (35 µg/l) (5).

4) Copper-Zinc (Cu = 130 µg/l; Zn = 400 µg/l; hardness 11 mg/l). Lake Orvsjoen, Norway (EIFAC 1976).

Fish are absent from this lake.

5) Copper-Zinc (Cu = 35 µg/l; Zn = 150 µg/l). River Skorovasselv (EIFAC 1976).

Brown trout and salmon have disappeared from this river; only sticklebacks were collected.

6) Copper-Zinc (ranges of station means were: Cu = 9.8-14.4 µg/l-control level was 6.6 µg/l; Zn = 95.8-134.1 µg/l-control level was 3.3 µg/l; hardness = 43.7-394.9-control level was 13.63; pH = 512-7.34-control was 7.34). Northwest Miramichi River System, New Brunswick (Cook et al. 1971, Saunders and Sprague 1967, Elson 1974, Pippy and Hare 1969). Note: Values cited are from Cook et al. 1971.

Although brook trout were present, Atlantic salmon avoided the South Tomogonops River and no lampreys or sticklebacks were collected from polluted sections. Fewer blacknose dace were found at polluted sites. It has been estimated that losses from the stock of salmon because of premature downstream movement and avoidance of spawning tributaries were about 15 to 18 percent.

A surge of copper and zinc because of a failure of pollution control devices caused death of some salmon and white suckers and weakened others. Debilitated fish were killed by an infection of Aeromonas liquefaciens, the epizootic having been promoted by high water temperature.

Note: Other factors such as logging and runoff containing pesticides and herbicides may also have been involved.

7) Copper-Zinc (see below for values). Several lakes receiving fallout from the Flin Flon smelters (Van Loon and Beamish 1977).

Fish populations (abundance, year-class strength, growth) were not affected in lakes with up to 10 µg Cu/l and 90 µg Zn/l. However, in Hammell Lake where average copper levels reached 9-15 µg/l and zinc levels average 300 µg/l (range 130-360 µg/l) reduced populations of white sucker, walleye, and lake whitefish were observed. Spawining white suckers was also impaired.

It was noted that populations were maintained in lakes with metal levels higher than levels that proved lethal in aquarium tests.

8) Copper-Zinc (Zn = 10-150 µg/l in summer; Cu = 1-40 µg/l; pH 3.9-6.0). Honnedaga Lake, New York (Schofield 1965).

Summer kills of brook trout were observed. Hatchery fish transplanted into the lake did not survive unless previously acclimated to high zinc levels. Low pH may be a factor influencing the availability of zinc, and there are indications that the lake water has lost much of its buffering capacity.

The joint effect of copper and zinc has been shown to be both additive and more than additive in acute experiments. More than additive effects occurred in soft waters (Table 42).

Fish were absent from a lake in which copper and zinc concentrations were 130 g/l and 400 g/l, respectively (4). Copper alone at that concentration could have caused the extinction of fish populations; the zinc contribution was probably small compared to the total toxicant (Tables 3 and 13).

The disappearance of brown trout and Atlantic salmon from a river containing 35 µg Cu/l and 150 µg Zn/l has been reported (4); however, sticklebacks were found in the river. In a chronic bioassay 43 µg Cu/l affected brown trout (Table 3) and Atlantic salmon were killed by 40 µg Cu/l. Copper by itself could have destroyed the salmon and trout populations. Applicable data on the toxicity of copper and zinc to sticklebacks are unavailable.

Kills of stocked brook trout occurred in a soft water lake in which copper and zinc levels varied from 1 to 40 µg/l and from 10 to 150 µg/l, respectively (8). While chronic effects on this species may occur at lower copper levels than the maximum value given above, zinc pollution would not appear to have been a problem. The existence of a natural brook trout population in the lake and the fact that acclimated hatchery fish were able to survive suggest that metal toxicity alone was not the cause of the fish kills. Reduction of pH, which dropped to levels as low as 3.9, probably contributed to the toxic effect (Table 37).

Saunders and Sprague (1967) observed that concentrations of copper and zinc approximately 0.4 times of the lethal levels (from laboratory tests) caused Atlantic salmon to avoid a river polluted by mine discharges (6). Avoidance has been demonstrated in the laboratory at lower copper and zinc concentrations (Pages 36 to 38), but laboratory tests cannot take into account all the factors which influence the success of a fish in ascending a spawning stream.

Populations of the white sucker, walleye, and lake whitefish declined, and spawning of white suckers was impaired in a lake containing 9-15 µg Cu/l and

300 µg Zn/l (7). No adverse effects on fish populations were seen in lakes with up to 10 µg Cu/l and 90 µg Zn/l, although effects at these concentrations could be inferred from the results of a chronic toxicity bioassay of a copper, and zinc mixture (Eaton 1973). Cadmium was also present in this test but did not appear to increase the toxicity.

Lead-Zinc--Lead-zinc pollution in Cardiganshire, England has been studied by several investigators. In many of these studies other trace metals were probably present but were not measured.

9) Lead-Zinc (Pb = 200-500 µg/l pH 6.4). River Rheidol, Cardiganshire (Carpenter 1924, 1925).

No fish were present in this river.

10) Lead-Zinc (Pb = trace to 300 µg/l). River Melindwr, Cardinganshire (Jones 1940)

Minnows (Phoxinus phoxinus) and brown trout (Salmo trutta) were present above the source of pollution but were absent below the source. Sticklebacks avoided the river.

11) Lead-Zinc (Pb = 400-500 µg/l; pH 6.4-6.8; no zinc levels given). River Ystwyth, Cardiganshire (Carpenter 1925).

Fish were absent from polluted stretches of the river.

12) Lead-Zinc (Pb = trace to 50 µg/l; Zn = 700-1200 µg/l; pH 6-6.4). River Ystwyth, Cardiganshire (Jones 1940b).

No fish were observed in the main channel of this river, despite reduced lead levels (see #11).

13) Lead-Zinc (Zn = 200-700 µg/l; lead no longer detected in water samples). River Ystwyth, Cardiganshire (Jones 1958).

Brown trout were now found in the river, indicating that some recovery had taken place.

A lead concentration of 31 µg/l was detrimental to brook trout; lake trout, rainbow trout, bluegills, channel catfish, and white suckers were affected at levels below 300 µg Pb/l in chronic experiments. All of the experiments were conducted in soft water. Rainbow trout were harmed at 850 µg Pb/l in hard water (Table 19). Further, zinc was chronically toxic to fathead minnows at concentrations below 300 µg Zn/l in hard and soft water. Chronic effects on trout species occurred between 500 and 1500 µg Zn/l (Table 13).

Carpenter (1924, 1935) stated that no fish were present in a river containing 200-500 µg/l Pb. Later, Reese (1937) measured high zinc concentrations in the same river. Fish were absent below sources of lead pollution (up to 300 µg/l) in another river, according to Jones (1940). Although no figures for hardness are available, Jones (1940) noted the lack of limestone among local rocks. We may assume, therefore, that the rivers contained soft water.

In a third river, polluted stretches containing 400-500 µg Pb/l were devoid of fish (Carpenter 1925). Fish were still absent in later years despite a decline of lead levels to 50 µg/l. However, zinc levels were measured and found to range from 700-1200 µg/l (Jones 1940b) levels which would be toxic to fish based on current bioassay data. Brown trout reappeared later when zinc levels had declined to less than 700 µg/l and lead was no longer detectable (Jones 1958).

Cobalt-Nickel--Little field data is available on the effects of cobalt or a cobalt-nickel mixture.

14) Cobalt-Nickel (Co 10-43 µg/l in winter, no other values were given; Ni was not consistently higher than controls; some Zn accumulated in sediments). Ricklea River, Sweden (Sodergren 1976).

A reduction in numbers of juvenile Atlantic salmon and brown trout was observed. Reduced numbers and species of insect larvae were also noted and the effects on fish could therefore have been caused by a reduced food source.

Cobalt was lethal to carp at 86 µg/l; a transitory effect on carp growth was observed at 50 µg Co/l (Table 22), so it is possible that the cobalt was responsible for the reduced populations of juvenile fish.

Mixtures of more than two metals--Two case studies are available where more than two heavy metals were present.

15) Copper-Zinc-Lead-Cadmium (max. values were: Cu = 400,000 µg/l; Zn = 900,000 µg/l; Cd - 3,000 µg/l; Pb = 25,000 µg/l). Clark Fork River, Montana (Van Meter 1974). Note: Metal levels are from Wood (1975).

Stretches of this river were barren of fish. The author felt this was primarily due to a heavy burden of calcareous silt which inhibited insect life. A reduction in the number of smolts and juvenile Salmo salar and S. trutta was observed. It was thought that this may have been the result of reduced insect populations.

16) Copper-Zinc-Lead (max. values were: Cu - 40 µg/l; Zn = 240 µg/l; Pb = less than 50 µg/l; soft water). Boulder River, Montana (Nelson 1976).

Decreased trout populations and biomass were found in the more heavily polluted stretches of this river. Cover was found to ameliorate some effects at lower metal concentrations.

The population size and biomass of rainbow trout and brook trout were

decreased in polluted stretches of a soft water river containing 40 µg Cu/l and 240 µg Zn/l. Lead concentrations ranged to as much as 100 µg/l but were often too low to measure. Both species can be affected by copper concentrations below 40 µg/l (Table 3), so copper alone could have produced the observed effects. Zinc and lead may have contributed toxicity to the river water, but to a lesser extent (Tables 13 and 19).

Levels of 400 mg Cu/l, 900 mg Zn/l, 3 mg Cd/l, and 25 mg Pb/l were found in stretches of a river reported by Van Meter (1974) to be devoid of fish (15). The presence of any of the four metals in such high concentrations would have destroyed fish populations, according to the laboratory toxicity tests results (Tables 3, 13, 16 and 19).

Low pH Case Studies-Bacteria, Decomposers and other Microorganisms

Natural bacterial populations are generally reduced in waters receiving acid precipitation or acid mine drainage. Toxicity may be exerted by several means. Sulphate is deleterious to heterotrophic microbes (Tutle et al. 1969). Extremes outside the pH range 5-8 are bacteriostatic (Cook and Wilson 1971). Anaerobic bacteria are inhibited by the positive oxidation-reduction potential created by oxididized metals (Tuttle et al. 1969 a,b). Acidification results in the progressive reduction of these bacteria. Sulphate-reducing bacteria are virtually eliminated at pH levels less than 5.5 (Tuttle et al. 1969, Whitesell et al. 1971). Other bacteria affected adversly by low pH are ammonia-oxidizers and non-acidophilic sulfur-oxidizers (Scheider et al. 1975).

The reduction in these bacterial populations results in reduced decomposition and nutrient cycling. Decreased decomposition caused by low pH (approximately 5) has been demonstrated experimentally (Leivestad et al. 1976) and has been

observed in the field (Almer et al. 1974, Grahn et al. 1974, Leivestad et al. 1976). Accumulation of organic detritus occurred in these studies. Anderson et al. (1975, cited in Leivestad et al. 1976) and Scheider et al. (1975) observed increased decomposition and microbial activity when lime was added to increase the pH of polluted waters.

A shift to pH tolerant organisms is observed in polluted waters. Chemosynthetic, autotrophic iron and sulfur bacteria, and some acidophilic aerobic bacteria typically dominate waters polluted by acid mine drainage (Collier et al. 1970, Cook and Wilson 1971, Millar 1973, Tuttle et al. 1968, 1969). Yeasts and fungi have been observed in streams polluted by acid mine drainage (Colmer and Hinkle, 1947, Cooke, 1966) and acid precipitation (Grahn et al. 1974). Any decomposition that takes place in acidified habitats is accomplished largely by these groups of organisms. The fungi may cause the flocculation of colloidal iron due to their mucilagenous secretions, but do not decrease the acidity of the water (Cooke 1966) and fungal mats may reduce mineral cycling by limiting the exchange with water (Grahn et al. 1974). Some yeasts may accelerate the decrease of environmental pH through metabolic activity (Tuttle et al. 1968).

Low pH Case Studies-Algae

Phytoplankton and periphyton are adversely affected by acidity. Chloroplast and chlorophyll structure may be affected and tolerant species inhabiting acidified waters exhibit cytological modifications that are thought to be survival adaptations (Bennett 1969). Reduced standing crop, number of species, and diversity and shifts in species composition toward a few acid-tolerant and acidophilous taxa, which may show increases in abundance have been

commonly observed (Almer et al. 1974, Bennett 1969, Conroy et al. 1975, Diehl 1972, Grahn et al. 1974, Johnson et al. 1970, Leivestad et al. 1976, Patrick et al. 1968, Rosso 1975, Stokes and Hutchinson 1975, Whitby et al. 1976, Yan 1975). Diversity in algal populations in strip-mine lakes has been positively correlated to increasing pH (see Nesler and Bachmann 1977).

Severe effects of acid appear to be most severe in the range of pH 5-6. Partick et al. (1968) observed large reductions in algal standing crop at pH 5.26, and significant reductions in the number of species at pH 5.0. Acidophilous periphyton species predominate at this pH (Besch et al. 1972). The greatest changes in species diversity occur withing this range (Almer et al. 1974).

In general, Cyanophyta, Chrysophyceae, Rhodophyta and Bacillarriophyceae have been observed to decline in acid waters, many species having been eliminated between pH 5 and 6 (e.g. Bennett 1969, Johnson et al. 1970 and references above). Some members of the Bacillariophyceae may be abundant at low pH and members of the Rhodophyta have been observed to increase in abundance at pH 4 to 5 (Conroy et al 1975). Acidic water communities are typically dominated by Chlorophyceae, although in some cases, near-elimination of this group has been observed at pH values near 5.8 (Almer et al. 1974, Johnson et al. 1970, Wollitz, 1972). Dinophyceae and Cryptophyceae have also been observed to increase in abundance at low pH (Yan 1975).

Alteration of phytoplankton communities is also noted in a change in the mean size of individual phytoplankers. An increase in the relative abundance of nanoplankton (Volkmar 1972) and a decrease in net plankton numbers (Bible 1972)

have been observed in acid waters. This size-change phenomenon was observed in acid strip mine lakes by Reed (1974, cited in Nesler and Bachmann 1977).

Alterations in primary productivity occur with changes in population structure. Lower rates of carbon fixation, (Conroy and Keller 1976, Johnson et al. 1970, Volkmar 1972) and diel oxygen curves (Rosso 1975) have been observed in acidified waters. Reductions have been attributed to the combined effects of reduced algal standing crop and lower inorganic carbon concentrations. Although rates of production are diminished, total production may be increased because of increased light penetration (Johnson et al. 1970, Volkmar 1972). Photosynthesis by benthic algae in waters receiving acid mine drainage is further inhibited by iron deposition (Carrithers and Bulow 1973, Koryak et al. 1972) and sedimentation (Collier et al. 1970) which eventually may smother the algae.

Although laboratory studies were not extensively reviewed, correlation with field observations seems to be good. Patrick et al. (1968) found decreases in standing crop andnumber of species of diatoms at pH levels of 5.2 and 5.0, respectively. Acidophilous species of diatoms were observed to be dominant in natural communities at the latter pH (Besch et al. 1972). It would be expected that more sensitive groups, such as Cyanophytes and Chrysophyceae would show effects at higher pH. Obvious changes in algal communities may be expected in the pH range 5-6.

LOW pH CASE STUDIES - MACROPHYTES

Low pH may be a factor in the absence, abundance and distribution of aquatic vascular plants. Moore and Clarkson (1967) found that variability in macrophyte communities was influenced by pH. Reductions in species diversity and production were observed near Sudbury, Ontario, where the numbers of

floating-leaved and submerged species were inversely related to dissolved sulphate concentrations (Gorham and Gordon 1963). Succession from Lobelia and Isoetes dominated communities to Sphagnum sp. communities has occurred in Scandanavian lakes receiving acid precipitation (Gralhn 1975).

The acid tolerant, floating-leaf Potamogeton americanus replaced the less tolerant, submerged-leaf P. foliosus as pH decreased in strip-mine lakes. The density of vegetation was observed to decrease with decreasing pH. Only emergent vegetation was found at pH levels below 6.4 (Bell 1956).

Plant growth and development may be affected by low pH. Growth of Lobelia at pH 4 was greatly reduced compared to pH 6. Limitation of plant growth may result from pH effects on essential minerals at this level. Eleocharis acicularis and sagittaria graminea did not reproduce sexually in acid water and the latter plant did not develop past the rosette stage (Clarkson and Moore 1971).

The effects of pH on aquatic macrophytes may be of secondary importance in some cases. Gorham and Gordon (1963) noted that the number of species present was low even at the relatively high pH of 6, and indicated that heavy metal pollution from the Sudbury smelters may have been involved.

Several other factors associated with acid mine drainage appear to have important inhibitory affects on aquatic plants: instability of the substrate, sedimentation (Collier et al. 1970, Roback and Richardson 1969), unstable water table (Bell 1956), high ionic concentration (Bell 1956), and steep-sloped shoreline reducing the littoral zone (Bell 1956, Maupin et al. 1954).

Low pH Case Studies - Zooplankton

Zooplankton populations are severely restricted by acid pollution. Lower diversity, numbers of species and standing crop result from decrease in pH (Almer et al. 1974, Parsons 1968, Sprules 1975). Mose daphnid chadocerans appear to be extremely sensitive to low pH being eliminated at about pH 6 (Almer et al. 1974). Copepods and rotifers dominate acid-stressed communities during periods when high-acid stress is presnet (Rosso 1975). Several studies have shown that pH of 5 appeared critical to zooplankton distribution, and the complexity of species associations (Bible 1972, Parsons 1968, Sprules 1975). Changes in species composition toward acid tolerant taxa have been noted (Parsons 1968, Rosso 1975, Sprules 1975).

Low pH Case Studies -Macroinvertebrates

Macroinvertebrates are adversely affected by low pH resulting from acid precipitation and acid mine drainage. Reduced biomass, density, number of species and species diversity, and a shift in species composition toward acid tolerant taxa are usually observed (Carrithers & Bulow 1973, Collier et al. 1970, Dills and Rogers 1974, Herrick and Cairns 1972, Leivestad et al. 1976, Nichols and Bulow 1973, Orciari and Hummon 1975, Parsons 1968, Roback and Richardson 1969, Rosso 1975, Simmons and Reed 1973, Sutcliffe and Carrick 1973, Tomkiewicz and Dunson 1977). In some cases, the density or abundance of tolerant organisms may be high (Conroy et al. 1975, Frost 1942, Koryak et al. 1972, Parsons 1968). In the majority of the reports cited, the most drastic reductions in diversity occur within the range of pH 5.7-6.0. Warner (1971) found a gradual reduction in diversity from pH 5.7 to 4.5, and a sharp reduction at 4.2.

Rapid recovery of macroinvertebrate populations generally occurs where temporary

or low-stress pollution exists (Cairns et al. 1971, Herrick and Cairns 1972, Parsons 1968, Roback and Richardson 1969, Rosso 1975, Simmons and Reed 1973). Diversity increases with improving water quality in both streams and acidified lakes (Campbell et al. 1965, Harp and Campbell 1967, Lind and Campbell 1970, Scheider et al. 1975, Smith and Frey 1971, Stickney and Campbell 1972, Stockinger and Hays 1960).

Species composition is shifted toward acid tolerant species. Amphipods are quite sensitive to acid pollution, resulting from acid mine drainage (Branson and Batch 1972, Koryak et al. 1972, Murpin et al. 1974, Rosso 1975) and acid precipitation (Conroy et al. 1975, Leivestad 1976, Okland 1970, Scheider et al. 1976, Sutcliffeand Carrick 1973). In Norway and Canada, the absence of Gammarus, an important forage organism for many fishes, has been observed at pH less than 6.

Molluscs are also sensitive organisms. They are generally the first populations to be eliminated by acid mine drainage and are the slowest to recover (Cairns et al. 1971, Dieffenback 1974, Parsons 1968, Rosso 1975, Simmons and Reed 1973). Molluscs are absent or rare in waters polluted by acid precipitation, where the pH is less than about 5.8 (Conroy et al. 1975, Grahn et al. 1974, Leivestad et al. 1976, Scheider et al. 1976, Sutcliffe and Carrick 1973).

Among the annelids, leeches appear to be the most sensitive (Conroy et al. 1975) while oligochaetes are quite resistant to acid pollution, frequently being dominant in communities at pH values of 4.5 and less. Abundance of oligochaetes may or may not be affected, although distribution is likely to be more uneven in certain cases such as in acid strip-mine lakes (Conroy et al. 1975, Hagen and Langeland 1973, Koryak et al. 1977, Leivestad 1976, Orciari and Hummon 1975, Roback and Richardson 1969, Scheider et al. 1976, Sutcliffe and Carrick 1973).

Ephemeroptera, Trichoptera, Plecoptera and Odonata are generally restricted by acid pollution, with reductions in species occurring between pH 5.5 and 6. A few members of Diptera (notably Chironomidae, Neuroptera, Megaloptera (Sialis sp) Coleoptera (especially Dysticidae), Hemiptera (Corixidae), Odonata and Trichoptera (Ptilostomis) appear quite resistant. Communities in severely polluted areas are frequently dominated by chironomids (Cairns et al. 1971, Carrithers and Bulow 1973, Collier et al. 1970, Conroy et al. 1975, Dieffenbach 1974, Dills and Rogers 1974, Hagen and Langeland 1973, Harrison 1962, Herrick and Cairns 1972, Grahn et al. 1974, Koryak et al. 1977, Leivestad et al. 1976, Nichols and Bulow 1973, Roback and Richardson 1969, Rosso 1975, Scheider et al. 1976, Sutcliffe and Carrick 1973, Tomkiewicz and Dunson 1977, Warner 1971). In some cases more serious effects on herbivorous than predatory insects have been noted (Sutcliffe and Carrick 1973, Grahn et al. 1974).

Other factors, especially pollution from mine drainage may influence the direction and magnitude of changes in species composition. Siltation, precipitation of iron, low oxygen tension and high free carbon dioxide, and changes in food organisms may contribute to the demise of organisms dependent on the substrate. Some hemiptera and Coleoptera may dominate the nonbenthic fauna because of their independence from substrate. Benthic organisms within the substrate, such as the larvae and pupae of many Diptera and Sialis sp.are unaffected by low pH stress. (Cairns et al. 1971, Herrick and Cairns 1972, Koryak et al. 1972, Parsons 1968, Roback and Richardson 1969).

Adverse effects on macroninvertebrates have been observed at rather high pH values in acute toxicity bioassays. Effects on some insects have been observed at pH 6.6 (Table 36). Members of Ephemeroptera and Plecoptera are quite sensitive with LC_{50} values having been greater than pH 5.7. Odonates were

inhibited at pH 5.2 and below, while Trichoptera were more resistant, effects were noted at pH values less than 5. In all groups, more resistant members were found. It should be noted that most laboratory data are from acute studies and adverse effects may be expected at higher pH levels. These results are generally compatible with observations in the field, where major changes in community structure have been found to occur in the pH range 5.7 to 6. Further, it was noted that within a given order, species can differ greatly in resistance to acid pollution.

Low pH Case Studies - Fishes

Adverse effects on fish populations resulting from acid precipitation have been well documented in Norway (Jensen and Snevik 1972), Sweden (Almer et al. 1974), Canada (Beamish 1974, Beamish 1975, Beamish et al. 1975, Harvey 1975) and the United States (Schofield 1976). Nesler and Bachmann (1977) cite several references relating fish kills and the decline of fish populations to acid mine drainage.

Different species are affected at various pH levels, and the disappearance of species is related to their tolerance of this stress. Reductions in species diversity and changes in species composition result as waters become acidified.

Acid precipitation has caused the acidification of workers in southern Norway and a decline of several fish populations has resulted. Many lakes are devoid of fish. The percentage of empty lakes was found to increase from 3.8 to 60 as the pH of the water decreased from 5.5 to 4.5. Salmon and sea trout runs have been declining for several years and are, at present, virtually nonexistent. The early decline of these species may have been the result of greater sensitivity to low pH stress or to avoidance behavior elicited by the stress. Although brown trout populations persisted somewhat longer, a decline has also been

observed, apparently because of recruitment failure. Perch and eels appear to be the most resistant species. These fish breed at sea, and the sensitive spawning and early growth stages are therefore not spent in acidified waters (Jensen and Snekuik 1972, Leivestad et al. 1976).

Almer et al. (1974) and Grahn et al. (1974) have reported the effects of acid precipitation on fish populations in Sweden. The pH of nearly 50 percent of the lakes in western Sweden is less than 6. Lakes in the central and eastern regions are affected to a lesser extent. Perch and eels were the most abundant species in lakes with pH within the range of 4.4 and 5.4. Although some pike were observed, populations were declining. Since tolerance to low pH stress differs, different species have become extinct as waters become more acidic. The general order of disappearance from Swedish lakes, and presumably of increasing tolerance is as follows: roach, minnow (Phoxinus phoxinus), arctic char, brown trout, cisco, perch, pike and eel. Tench and carp are extinct in most areas of western Sweden.

Few fish remain in the lakes of the La Cloche Mountain region, which receives acid precipitation from the smelters at Sudbury. Fish are absent from many of these lakes. The numbers of species present in lakes has been shown to be significantly correlated to pH. Smallmouth bass, walleye, burbot and lake trout populations disappeared at pH levels of 5.8 to 5.2. Northern pike, pumkinseed, white suckers, brown bullhead, and rock bass were eliminated from waters when the pH dropped to 5.2 to 4.7. Perch, lake herring and some cyprinids (lake chub) still spawned at pH's between 4.5 and 4.8. All fish were eliminated in lakes with a pH of less than 4.5. Failure to spawn apparently led to the demise of these populations (Beamish 1974, 1975, Beamish and Harvey 1972, Beamish et al. 1975, Harvey 1975).

In the eastern United States, 51 percent of the lakes in the Adirondock region have a pH of less than 5. Ninety-percent of these lakes were found to be devoid of fish (Schofield 1976).

Acid pollution resulting from mine drainage has resulted in similar affects. Various reports indicate that fish are absent from streams or strip-mine lakes when the pH is between 4.5 and 5, and several species are affected at pH levels up to 6.5 (Buthler et al. 1973, Dahl 1963, Harrison 1962, Koryak et al. 1972, Nichols and Bulow 1973, Parsons 1968, Warner 1971).

In waters that gradually become acidic, the reported decline of fish populations results from recruitment failure. This may occur because of the failure of fish to spawn (Beamish et al. 1975) and/or because of increased egg, fry and fingerling mortality (Johansson et al. 1973, Leivestad et al. 1976). Stressed populations are typically composed of older, larger fish (Beamish et al. 1975, EIFAC 1969, Leivestad et al. 1976).

Large or rapid changes in pH appear to be even more detrimental to the persistence of fish populations. Excessive acidity may occur during spring snow melt, periods of heavy precipitation and periods of high discharge of acid mine wastes. Many fish species spawn in the spring and the especially sensitive egg and fry stages may be exposed to sudden pH decreases. Kills of older fish have been observed at these times (Dahl 1963, Hultberg 1975).

The growth of individual fish is generally reduced in acid waters (Beamish 1974, Frost 1939). This may not be caused by a lack of food, but rather by decreased feeding intensity or food utilization (Beamish et al. 1975). In some cases, however, depletion of food organisms may contribute to the decreased growth rates observed in fish inhabiting acidic waters (Branson and Batch 1972, Okland 1969). In some cases, increased growth of some species occurs as

competition from more sensitive species is reduced (Beamish et al. 1975, Leivestad et al. 1976, Milbrink and Johansson 1976).

Other factors associated with acid precipitation and acid mine drainage that contribute to fish mortality are: heavy metals, increased free Co_2, iron deposition and siltation (Beamish 1974, Branson and Batch 1972, Carrithers and Bulow 1973, Dahl 1963, Mount 1973, Nichols and Bulow 1973).

Generally, good correlation between laboratory and field studies has been observed. A few cases where comparable data exist will be cited. Deleterious effects on white suckers were observed in laboratory tests at pH 5.3, and effects on populations were observed in lakes with pH 4.7-5.2. Northern pike appear to be quite resistent to acid pollution, showing effects in laboratory studies at pH 4.2. This value may be considerably higher, around 5.0 (see table 38), which agrees well with data from Swedish lakes (Milbrink and Johansson, 1975). These authors and Beamish (1974, 1975) have noted good general correlations between bioassay results and field observations for other species.

EIFAC (1969) cites several examples of fish populations existing in waters with pH less than 5 and considers pH from 5 to 9 as "safe" for fish populations. In view of the severe effect that have been noted in other instances, such as the many empty lakes with pH 5.5 and lower and the disappearance of several species at pH values of 5.8 and less, this estimate would seem to be somewhat low. A pH of 6 would permit the survival and adequate production of most species.

The early disappearance of migatory fish, such as salmon and sea trout, from Swedish rivers (Jensen and Snevik, 1972) may be due to reproductive

failure at lowered pH. However, avoidance of acidic rivers cannot be ruled out. It is possible then, that fish that migrate upstream to spawn may suffer in this manner as spawning grounds are polluted, even though the habitat they occupy as adults may be tolerable.

SUMMARY

The data on the toxicity of heavy metals, ore benefification reagents, and hydrogen ion compiled from bioassays and case studies reported in the literature were summarized in Figures 1-11. These summaries provide a method to determine levels at which impact may begin to occur although actual detection could be impossible because of the natural variability in aquatic systems.

In summarizing the data presented in this report it is evident that a great deal of variability exists in the critical levels from various stress studies. This variability is the result of different species being studied, variable physical and chemical test conditions, lack of control stations in field studies, and various combinations of stress.

Also, in many of the field studies, a number of metals are present but only one or two metals were usually measured. A lack of data on experimental levels of hardness, alkalinity, pH and TOC is another factor which causes difficulty in interpreting current data on heavy metal toxicity. For these reasons the stress charts were constructed to indicate ranges where impacts might begin.

In the case of metals, and ore beneficiation reagents orders of magnitude were used to indicate ranges where impacts might be expected. In some cases, the ranges present a conservative estimate of where impacts may begin; these are used only as indicators of need for further analysis. The groups

of organisms affected in various ranges are indicated on the charts as are the levels obtained from the current bioassays.

The effects of low pH were summarized to indicate levels where changes have been observed in the field or laboratory. Where contradictory data exist, the lowest reported level is indicated on the figure.

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Table 1. Toxicity of Copper to Freshwater Rotifers and Protozoans

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
700*	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974
1000*	protozoan community	39% mean reduction in number of species after 1-day exposure. 12% reduction at 500 µg Cu/liter, the lowest treatment level tested.	NA	NA	NA	NA	Ruthven and Cairns 1973
1100*	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.8	81	54-67	Buikema et al. 1974

NOTE: *nominal value

Table 2. Toxicity of Copper to Freshwater crustaceans

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
5*	cladoceran Daphnia hyalina adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
8	amphipod Gammarus pseudolimnaeus adults (second generation)	No survival after 9-week exposure. Survival similar to control at 5 µg Cu/liter. Test animals were produced in Cu solutions by parents which had been exposed to Cu for 6 weeks.	15	7.7	45	43	Arthur and Leonard 1970
10	cladoceran Daphnia magna	2-day LC50. Cu exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed. Presence of food increased LC50 to 60 µg Cu/liter.	18	7.7	45	42	Biesinger and Christenson 1972
15	amphipod Gammarus pseudolimnaeus adults (first generation)	Reduced survival and no growth after 6-week exposure. Survival and growth rate similar to control at 8 µg Cu/liter. Test animals were adults at beginning of experiment.	15	7.7	45	43	Arthur and Leonard 1970
30*	crayfish Orconectes rusticus juveniles	Growth rate 9% as great as in control during 30-day exposure. Growth rate 72% of control at 15 µg Cu/liter. Cu exposure began with newly hatched young.	20	7.8-8.1	100-125	NA	Hubschman 1967
35	cladoceran Daphnia magna adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
44	cladoceran Daphnia magna adults	21-day LC50. Cu exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly	18	7.7	45	42	Biesinger and Christenson 1972

Table 2. continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
60	cladoceran *Daphnia ambigua*	Significant reduction in instantaneous rate of population growth. No significant reduction at 40 µg Cu/liter. Cu exposure began with animals less than 1 day old. Test solutions were renewed and test animals were fed every 3 days. Young were counted and discarded daily; test continued until all original animals were dead.	20	8.2-9.5	130-160	100-119	Winner and Farrell 1976
60	cladoceran *Daphnia parvula*	No reproduction. No significant reduction in instantaneous population growth rate at 40 µg Cu/liter. Cu exposure began with animals less than 1 day old. Test solutions were renewed and test animals were fed every 3 days. Young were counted and discarded daily; test continued until all original animals were dead.	20	8.2-9.5	130-160	100-119	Winner and Farrell 1976
60	cladoceran *Daphnia pulex*	Significant reduction in instantaneous rate of population growth. No significant reduction at 40 µg Cu/l. Cu exposure began with animals less than 1 day old. Test solutions were renewed and test animals were fed every 3 days. Young were counted and discarded daily; test continued until all original animals were dead.	20	8.2-9.5	130-160	100-119	Winner and Farrell 1976
80	cladoceran *Daphnia magna*	Significant reduction in instantaneous rate of population growth. No significant reduction at 60 µg Cu/l. Cu exposure began with animals less than 1 day old. Test solutions were renewed and test animals were fed every 3 days. Young were counted and discarded daily; test continued until all original animals were dead.	20	8.2-9.5	130-160	100-119	Winner and Farrell 1976
500*	copepod *Eudiaptomus padanus* adults	2-day LC50. Test solutions were not renewed; test animals were no fed.	10	7.2	33	29	Baudouin and Scoppa 1974

Table 2 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
1200	isopod Asellus meridianus	2-day LC50. Test solutions were not renewed; test animals were not fed.	20	NA	25	NA	Brown 1976
2500*	copepod Cyclops abyssorum adults	2-day LC50. Test solutions were not renewed; test animals were not fed. NOTE: *nominal value	10	7.2	33	29	Baudouin and Scoppa 1974

Table 3. Toxicity of Copper to Freshwater Molluscs

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
13*	snail *Physa heterostropha* juveniles	4-day LC50. Test solutions were not renewed; test animals were not fed. Addition of food increased LC50 to 53 µg Cu/liter.	21	7.8	100	NA	Wurtz 1962
15	snail *Campeloma decisum*	Reduction in survival after 6-week exposure. No reduction at 8.0 µg Cu/liter. Snails were 11 to 27 mm in length at beginning of exposure. No observable growth in treatments or controls.	15	7.7	45	43	Arthur and Leonard 1970
15	snail *Physa integra*	No growth during 6-week exposure. Growth rate similar to control at 8.0 µg Cu/liter. Snails were 4 to 7 mm in length at beginning of exposure.	15	7.7	45	43	Arthur and Leonard 1970
16*	snail *Physa heterostropha* juveniles	4-day LC50. Test solutions were not renewed; test animals were not fed. Addition of food increased LC50 to 34 µg Cu/liter.	21	7.3	20	NA	Wurtz 1962
28	snail *Physa integra*	Reduced survival after 6-week exposure. Survival similar to control at 14.8 µg Cu/liter.	15	7.7	45	43	Arthur and Leonard 1970
69*	snail *Physa heterostropha* adults	4-day LC50. Test solutions were not renewed; test animals were not fed.	21	7.8	100	NA	Wurtz 1962

NOTE: *nominal value

Table 4. Toxicity of Copper to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
14	midge *Tanytarsus dissimilis* larvae	Significant reduction in growth rate, measured by length and by head capsule width. Cu exposure began with embryos less than 16 hr. old, continued for 10 days, by which time larvae were in third instar. Test solutions were not renewed; test animals were fed on first day.	22	7.5-7.7	47-51	NA	Anderson et al. 1977
16	midge *Tanytarsus dissimilis* larvae	10-day LC50. Cu exposure began with embryos less than 16 hr. old. Larvae were in third instar after 10 days.	22	7.5-7.7	47-51	NA	Anderson et al. 1977
190	mayfly *Ephemerella grandis* nymphs	14-day LC50.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
320*	mayfly *Ephemerella subvaria* nymphs	2-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
8300*	stonefly *Acroneuria lycorias* nymphs	4-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
12000	stonefly *Pteronarcys californica* nymphs	14-day LC50.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
32000*	caddisfly *Hydropsyche betteni* larvae	50% survival after 14 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969

NOTE: *nominal value

Table 5. Toxicity of Copper to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
5	brook trout Salvelinus fontinalis juveniles	Significantly lower weight than in controls. Lowest treatment level employed. Survival significantly reduced at 27 µg/liter, but not at 13 µg/liter or lower. Cu exposure began 35 days before hatch, continued another 60 days.	10	6.6-7.1	38	28	Sauter et al. 1976
8	brook trout Salvelinus fontinalis juveniles	Significantly lower weight than in controls. No significant reduction at 5 µg/liter Cu. Survival significantly reduced at 49 µg/liter, but not at 21 µg/liter or lower. Cu exposure began 35 days before hatch, continued another 60 days.	10	6.7-7.1	187	178	Sauter et al. 1976
13	brook trout Salvelinus fontinalis embryos	Significant reduction in hatchability. No significant reduction at 7 µg/l Cu. Cu exposure began within one day after fertilization (35 days before hatch).	10	6.6-7.1	38	28	Sauter et al. 1976
17	brook trout Salvelinus fontinalis juveniles	Complete mortality within 11 months after hatch. Survival similar to control at 9.5 µg/liter Cu. Whether or not parents had been exposed to Cu did not affect survival. Growth rate also markedly depressed while fish survived. Application factor = 0.095 - 0.174	6-10 Lowest tested	7.5	45	42	McKim and Benoit 1971
18	fathead minnow Pimephales promelas juveniles	Complete mortality after 60 days. No significant reduction in survival at 10.6 µg/liter Cu. Cu exposure began at hatch. Application factor = 0.13 - 0.22	24-25	7.1	31	30	Mount and Stephan 1969
18	fathead minnow Pimephales promelas adults	No spawning and 50 percent mortality among fish exposed for 9 months. Survival and egg production at 11 µg/l Cu was similar to that in controls. Application factor = 0.13 - 0.22	19-25 Lowest tested	7.1	31	30	Mount and Stephan 1969
18	bluntnose minnow Pimephales notatus adults	Egg production significantly reducted. Lowest treatment level employed. Fish had been exposed to Cu for 14 mos.	25	7.9-8.3	194	165	Horning and Neiheisel 1977

Table 5 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
18	channel catfish Ictalurus punctatus juveniles	Significant reduction in survival. No significant reduction at 12 µg/liter Cu. Growth in weight, survival as embryos not significantly affected at any concentration tested (24 µg/liter and below). Cu exposure began within 3 days after fertilization (6-8 days before hatch), continued another 60 days after hatch.	22	7.4-7.6	36	34	Sauter et al. 1976
19	channel catfish Ictalurus punctatus juveniles	Significant reduction in survival and significantly lower weight than in controls. No significant effect on either parameter at 13 µg Cu/liter. Embryo survival not significantly affected at any concentration tested (66 µg/liter and below). Cu exposure began within 3 days after fertilization (6-8 days before hatch), continued another 60 days after hatch.	22	7.5-7.9	186	173	Sauter et al. 1976
32	rainbow trout Salmo gairdneri juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 11 µg Cu/l. Cu exposure began 11 days before hatch, continued 35 more days.	11	7.3-	45	42	McKim et al. 1977
33	brook trout Salvelinus fontinalis embryos	Hatchability significantly reduced. No significant reduction at 17.4 µg/liter Cu. Parents had been exposed to similar Cu concentrations for 22 months.	4-21 seasonal	7.5	45	42	McKim and Benoit 1971
33	fathead minnow Pimephales promelas adults	No spawning among fish exposed for 11 months. Egg production at 15 µg Cu/liter was similar to that in controls. Application factor = 0.03 - 0.07.	16-26 seasonal	7.9	198	161	Mount 1968

Table 5 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
34	white sucker *Catostomus commersoni* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 13 µg Cu/liter. Cu exposure began 13 days before hatch, continued 27 more days.	15	7.3-7.9	45	42	McKim et al. 1977
40	bluegill *Lepomis macrochirus* fry	Survival significantly reduced after 90 days. No significant reduction at 21 µg/liter. Application factor = 0.02 - 0.04.	23-28	7-8	45	43	Benoit 1975
42	lake trout *Salvelinus namaycush* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 22 µg Cu/liter. Cu exposure began 27 days before hatch, continued 66 more days.	6	7.3-7.9	45	42	McKim et al. 1977
43	brown trout *Salmo trutta* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 22 µg Cu/liter. Cu exposure began 72 days before hatch, continued 55 more days.	6	7.3-7.9	45	42	McKim et al. 1977
44	brook trout *Salvelinus fontinalis* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 22 µg Cu/liter. Cu exposure began 16 days before hatch, continued 60 more days.	6	7.3-7.9	45	42	McKim et al. 1977
74	brook trout *Salvelinus fontinalis* embryos	Significant reduction in hatchability. No significant reduction at 49 µg/liter Cu. Cu exposure began within one day after fertilization (35 days before hatch).	10	6.7-7.1	187	178	Sauter et al. 1976

Table 5 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
104	northern pike Esox lucius juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 35 µg Cu/liter. Cu exposure began 6 days before hatch, continued another 34 days.	16	7.3-7.9	45	42	McKim et al. 1977
162	bluegill Lepomis macrochirus adults	No spawning among fish exposed for 22 months. Normal spawning at 77 µg/liter.	13-28 seasonal	7-8	45	43	Benoit 1975
119	bluntnose minnow Pimephales notatus juveniles	Significant reduction in survival rate and mean weight. No significant reduction in either parameter at 72 µg Cu/liter. Cu exposure began at hatch, continued another 60 days.	25	7.9-8.3	194	165	Horning and Neiheisel 1977
225	rainbow trout Salmo gairdneri juveniles	Growth rate initially reduced relative to controls, but returned to near control rates after 40-day exposure at each of two different ration levels. Concentration equals 0.511 of 4-day LC50.	10	7.8-8.2	360-369	227	Lett et al. 1976

Table 6. Toxicity of Nickel to Freshwater Crustaceans and Rotifers

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
95	cladoceran *Daphnia magna* adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
130	cladoceran *Daphnia magna* adults	21-day LC50. Ni exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
510	cladoceran *Daphnia magna*	2-day LC50. Ni exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed. Presence of food increased LC50 to 1120 µg Ni/liter.	18	7.7	45	42	Biesinger and Christenson 1972
1900*	cladoceran *Daphnia hyalina* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
3600*	copepod *Eudiaptomus padanus* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
4900*	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974
15000*	copepod *Cyclops abyssorum* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974

NOTE: *nominal value

Table 7. Toxicity of Nickel to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
130	midge *Tanytarsus dissimilis* larvae	Significant reduction in growth rate, measured by length and by head capsule width. Ni exposure began with embryos less than 16 hr. old, continued for 10 days, by which time larvae were in third instar. Test solutions were not renewed; test animals were fed on first day.	22	7.5-7.7	47-51	NA	Anderson et al.
4000*	mayfly *Ephemerella subvaria* nymphs	4-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
64000*	caddisfly *Hydropsyche betteni* larvae	Greater than 50% survival after 14 days. No higher treatment levels were employed. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
33500*	stonefly *Acroneuria lycorias* nymphs	4-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969

NOTE: *nominal value

Table 8. Toxicity of Nickel to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
730	fathead minnow *Pimephales promelas* embryos	Significant reduction in hatchability. No significant reduction at 380 µg Ni/liter. Embryos were spawned in Ni solutions by fish exposed to Ni beginning at 6 weeks of age. Application factor = 0.014 - 0.027.	22-27	7.8	210	161	Pickering 1974
730	fathead minnow *Pimephales promelas* adults	Significant reduction in number of eggs produced per spawning. No significant reduction at 380 µg Ni/liter. Fish had been exposed to Ni beginning at 6 weeks of age. Application factor = 0.014 - 0.027.	13-27 Seasonal	7.8	210	161	Pickering 1974
4880*	fathead minnow *Pimephales promelas* juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed.	25	7.5	20	18	Pickering and Henderson 1966
5270*	bluegill *Lepomis macrochirus* juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed.	25	7.5	20	18	Pickering and Henderson 1966
32000*	rainbow trout *Salmo gairdneri* yearlings	2-day LC50. Test solutions were renewed at 6-hr intervals; test fish were not fed.	15.3-18.4	7.3-7.5	240	NA	Brown and Dalton 1970
39600*	bluegill *Lepomis macrochirus* juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed.	25	8.2	360	300	Pickering and Henderson 1966
43450*	fathead minnow *Pimephales promelas* juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed.	25	8.2	360	300	Pickering and Henderson 1966

NOTE: *nominal value

Table 9. Toxicity of Zinc to Freshwater Rotifers and Protozoans

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
1250*	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974
5000*	protozoan community	38% mean reduction in number of species after 1-day exposure. No reduction at 1000 µg Zn/liter.	NA	NA	NA	NA	Ruthven and Cairns 1973

NOTE: *nominal value

Table 10. Toxicity of Zinc to Freshwater Crustaceans

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
40*	cladoceran Daphnia hyalina adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
100	cladoceran Daphnia magna	2-day LC50. Zn exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed. Presence of food increased LC50 to 280 µg Zn/liter.	18	7.7	45	42	Biesinger and Christenson 1972
102	cladoceran Daphnia magna adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
158	cladoceran Daphnia magna adults	21-day LC50. Zn exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
500*	copepod Eudiaptomus padanus adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
5500*	copepod Cyclops abyssorum adults	2-day LC50. Test solutions were not renewed; test animals were not fed. NOTE: *nominal value	10	7.2	33	29	Baudouin and Scoppa 1974

Table 11. Toxicity of Zinc to Freshwater Molluscs

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
434*	snail Physa heterostropha juveniles	4-day LC50. Test solutions were not renewed; test animals were fed.	20	7.3	20	NA	Wurtz 1962
1110*	snail Physa heterostropha adults	4-day LC50. Test solutions were not renewed; test animals were not fed.	21	7.3	20	NA	Wurtz 1962
1270*	snail Heliosoma campanulatum adults	4-day LC50. Test solutions were not renewed; test animals were not fed. Identical LC50 in water of 100 µg/liter hardness.	23	7.3	20	NA	Wurtz 1962
1390*	snail Physa heterostropha juveniles	4-day LC50. Test solutions were not renewed; test animals were fed.	20	7.8	100	NA	Wurtz 1962
3160*	snail Physa heterostropha adults	4-day LC50. Test solutions were not renewed; test animals were not fed.	21	7.8	100	NA	Wurtz 1962
		NOTE: *nominal value					

Table 12. Toxicity of Zinc to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
9200	mayfly Ephemerella grandis nymphs	Greater than 50% survival after 14 days.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
13900	stonefly Pteronarcys californica nymphs	Greater than 50% survival after 14 days.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
16000*	mayfly Ephemerella subvaria nymphs	50% survival after 10 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
32000*	caddisfly Hydropsyche betteni larvae	50% survival after 11 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
32000*	stonefly Acroneuria lycorias nymphs	50% survival after 14 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969

NOTE: *nominal value

Table 13. Toxicity of Zinc to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
145	fathead minnow *Pimephales promelas* embryos	Significantly reduced adhesiveness to substrate and reduced chorion strength. No significant effects at 78 µg Zn/liter. Embryo hatchability significantly reduced at 295 µg/liter, but not at 145 µg/liter. Parents exposed to Zn since before hatch. Application factor = 0.13 - 0.24.	25	7-8	46	41	Benoit and Holcombe 1977
180	fathead minnow *Pimephales promelas* adults	Egg production markedly reduced. Lowest treatment level tested. Fish were exposed to Zn for 10 months. Application factor less than 0.02.	15-25 Seasonal	7.7	203	162	Brungs 1969
295	fathead minnow *Pimephales promelas* juveniles	Survival significantly reduced. No significant reduction at 145 µg Zn/liter. Mean weight of fish not affected at highest Zn level tested (576 µg/liter). Zn exposure continued for 8 weeks after hatch. Whether or not parents had also been exposed to Zn did not affect results.	25	7-8	46	41	Benoit and Holcombe 1977
500-600	Atlantic salmon *Salmo salar* sac fry, fingerlings (fg)	21-day LC50 for both life stages.	10 (fry) 15 (fg)	6.4	8	NA	Grande 1967
547	rainbow trout *Salmo gairdnerii* adults	64% mortality, probably after 21 months. Most mortality took place after fry had begun to feed. 23% and 10% mortality at 260 µg Zn/liter and 11 µg Zn/liter (control) respectively. Zn exposure began 6 weeks before hatch.	12.7	6.8	26	25	Sinley et al. 1974

Table 13 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
640	rainbow trout Salmo gairdnerii adults	6.4% mortality after 21 months. Probably statistically significant since no mortality occurred in lower concentrations and control, 10% amd 23% mortality, respectively, at 1055 and 2200 µg Zn/liter. Exposure began with 2-gram fingerlings. No spawning occurred in treatments or control.	16.2	7.8	333	238	Sinley et al. 1974
800-900	brown trout Salmo trutta sac fry	21-day LC50.	10	6.4	8	NA	Grande 1967
800-900	rainbow trout Salmo gairdneri sac fry	21-day LC50.	10	6.4	8	NA	Grande 1967
1300	fathead minnow Pimephales promelas juveniles	Significant reduction in survival after 20 days. No significant reduction at 660 µg Zn/liter. Zn exposure began within 1 day after fertilization.	15-25 Seasonal	7.7	203	162	Brungs 1969
1360	brook trout Salvelinus fontinalis embryos	Significant reductions in chorion strength and embryo hatchability. No significant reduction in either parameter at 534 µg Zn/liter. Embryos were spawned in Zn solutions by fish which had been exposed 4 months to Zn. Similar effects were observed for embryos spawned by unexposed parents. Application factor = 0.27 - 0.68.	9	7.0-7.7	45	42	Holcombe et al. 1977

Table 13 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
1368	brook trout Salvelinus fontinalis juveniles	Significant reduction in survival rate. No significant reduction at 717 µg Zn/liter. Test fish had been exposed to Zn since 6 hr after fertilization. Growth rate was not affected at concentrations permitting survival. Application factor = 0.27 - 0.68. In another test conducted under similar conditions, except that parents had been exposed to Zn, survival rate of juveniles was not significantly reduced at 1368 µg Zn/liter, the highest concentration tested.	9	7.0-7.7	45	42	Holcombe et al. 1977
1630	fathead minnow Pimephales promelas larvae	12-day LC50. Zn exposure began within 1 day after fertilization, continued until 3 days after hatch.	20	7.5-7.6	174-198	44-58	Pickering and Vigor 1965
4600	coho salmon Oncorhynchus kisutch parr	4-day LC50. Test solutions were renewed daily.	12	6.8-7.9	95	66	Lorz and McPherson 1976
4600	rainbow trout Salmo gairdneri juveniles	7-day LC50.	14.5-15.8	7.3-7.9	290	230	Ball 1967

Table 14. Toxicity of Cadmium to Freshwater Crustaceans and Rotifers

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
1	cladoceran Daphnia magna adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
4*	cladoceran Daphnia galeata mendotae	Significant reduction in numbers and biomass. No significant reduction at 2 µg Cd/liter. Laboratory populations were exposed to Cd for 23 weeks. Test solutions were renewed daily; test animals were fed daily.	Lake Michigan water; no physicochemical data reported				Marshall 1976
5	cladoceran Daphnia magna adults	21-day LC50. Cd exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
5*	Lake Michigan planktonic crustacean community	Significant reduction in total abundance, species diversity and community similarity. No lower treatment levels tested. Opaque carboys containing Cd solutions were suspended in epilimnion, incubated 4 to 15 days with no feeding or solution renewal during test period.	Northern Green Bay, Lake Michigan, summer, 1976.				Marshall and Van Reken 1976
55*	cladoceran Daphnia hyalina adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
65	cladoceran Daphnia magna	2-day LC50. Cd exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed.	18	7.7	45	42	Biesinger and Christenson 1972

Table 14 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
300*	rotifer Philodina acuticornis mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974
300*	rotifer Philodina acuticornis mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.8	81	54-67	Buikema et al. 1974
3800*	copepod Cyclops abyssorum adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 197

NOTE: *nominal value

Table 15. Toxicity of Cadmium to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
2000*	mayfly *Ephemerella subvaria* nymphs	4-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
10000	crane fly *Hexatoma sp.* larvae	80% survival after 21 days.	10	7.8	NA	240	Clubb et al. 1975
10000	snipe fly *Atherix variegata* larvae	No mortality after 21 days.	10	7.8	NA	240	Clubb et al. 1975
14000	stonefly *Pteronarcys californica* nymphs	No mortality after 14 days.	10	7.8	NA	240	Clubb et al. 1975
17500	stonefly *Pteronarcella badia* nymphs	30% survival after 7 days. 4-day LC50 = 28000 µg Cd/l.	10	7.8	NA	240	Clubb et al. 1975
17500	mayfly *Ephemerella grandis* nymphs	50% survival after 7 days. 4-day LC50 = 28000 µg Cd/l.	10	7.8	NA	240	Clubb et al. 1975
17500	stonefly *Acroneuria pacifica* nymphs	10% survival after 21 days.	10	7.8	NA	240	Clubb et al. 1975

Table 15 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
17500	stonefly Arcynopteryx signata nymphs	10% survival after 21 days.	10	7.8	NA	240	Clubb et al. 1975
32000*	caddisfly Hydropsyche betteni larvae	50% survival after 10 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
32000*	stonefly Acroneuria lycorias nymphs	50% survival after 14 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
42500	caddisfly Brachycentrus americanus larvae	No mortality after 7 days.	10	7.8	NA	240	Clubb et al. 1975
42500	crane fly Holorusia sp. larvae	50% survival after 7 days.	10	7.8	NA	240	Clubb et al. 1975

NOTE: *nominal value

Table 16. Toxicity of Cadmium to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
3	brook trout *Salvelinus fontinalis* adults	Complete mortality of males at beginning of spawning period. No Cd-caused mortality at 2 µg Cd/liter. Exposure began with yearling fish, 6 months before spawning began. Some eggs were fertilized at the lethal concentration, and effect described above occurred again with progeny, which were exposed 2 yr before they began to spawn. Growth rates of 2nd and 3rd generation fish were markedly reduced at this concentration.	9	7-8	44	43	Benoit et al. 1976
4	brook trout *Salvelinus fontinalis* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 1 µg Cd/l. Exposure began 24 days before hatch, continued another 126 days. Toxicant exerted effects mostly after hatch.	9.7	7.6	45	41	Eaton et al. 1977
4	brown trout *Salmo trutta* juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 1 µg Cd/l. Exposure began 2 days before hatch, continued another 61 days. Toxicant exerted effects mostly after hatch.	10	7.6	45	41	Eaton et al. 1977
6	brook trout *Salvelinus fontinalis* juveniles	Mean weight and survival rate significantly reduced. No significant reduction in either parameter at 3 µg Cd/l. Exposure began within 1 day after fertilization (35 days before hatch), continued until 60 days after hatch.	10	6.5-7.2	37	30	Sauter et al. 1976
12	brook trout *Salvelinus fontinalis* juveniles	Mean weight and survival rate significantly reduced. No significant reduction in either parameter at 7 µg Cd/l. Exposure began within 1 day after fertilization (35 days before hatch), continued until 60 days after hatch.	10	6.7-7.1	188	177	Sauter et al. 1976

Table 16 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
12	brown trout Salmo trutta juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 50 days before hatch, continued another 60 days. Toxicant exerted effects mostly after hatch.	10	7.6	45	41	Eaton et al. 1977
12	lake trout Salvelinus namaycush juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 10 days before hatch, continued another 64 days. Toxicant exerted effects mostly after hatch.	10	7.6	45	41	Eaton et al. 1977
12	white sucker Catostomus commersoni juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 10 days before hatch, continued another 30 days. Toxicant exerted effects mostly after hatch.	18	7.6	45	41	Eaton et al. 1977
13	coho salmon Oncorhynchus kisutch juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 20 days before hatch, continued another 62 days. Toxicant exerted effects mostly after hatch.	10	7.6	45	41	Eaton et al. 1977
13	northern pike Esox lucius juveniles	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 7 days before hatch, continued another 28 days. Toxicant exerted effects mostly after hatch.	16	7.6	45	41	Eaton et al. 1977

Table 16 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
13	smallmouth bass *Micropterus dolomieui*	Significant reduction in standing crop (no. of survivors X mean weight). No significant reduction at 4 µg Cd/l. Exposure began 3 days before hatch, continued another 30 days. Toxicant exerted effects mostly after hatch.	20	7.6	45	41	Eaton et al. 1977
17	channel catfish *Ictalurus punctatus* juveniles	Significant reduction in mean weight. No significant reduction at 12 µg Cd/liter. Survival significantly reduced at 59 µg Cd/liter, but not at 33 µg Cd/liter. Cd exposure began 2-3 days after fertilization (6-8 days before hatch), continued 60 days after hatch.	22	7.7-7.8	185	172	Sauter et al. 1976
20	channel catfish *Ictalurus punctatus* juveniles	Significant reduction in survival. No significant reduction at 17 µg Cd/liter. Growth in weight not significantly reduced at any concentration permitting survival. CD exposure began 2-3 days after fertilization (6-8 days before hatch), continued 60 days after hatch.	22	7.5-7.6	37	34	Sauter et al. 1976
57	fathead minnow *Pimephales promelas* embryos	Significant reduction in hatchability. No significant reduction at 27 µg Cd/liter. Embryos were spawned in Cd solutions by adults which had been exposed to Cd since 3 weeks after hatch. Application factor = 0.005 - 0.008.	23	7.6	204	154	Pickering and Gast 1972
80	bluegill *Lepomis macrochirus* adults	31% mortality, concurrent with spawning activity. No mortality in control or at 31 µg Cd/liter; 75% mortality at 239 µg/liter. Cd exposure began with yearling fish and continued 11 months.	16-29 Seasonal	7.7	207	152	Eaton 1974

Table 16 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
80	largemouth bass *Micropterus salmoides* juveniles	50% mortality after 82 days. 12.5% mortality after 6 months at 8 µg Cd/liter. Growth rate of survivors not significantly affected by Cd. Flow-through exposure system not employed. Chloride and sulfate concentrations in test water were 193 mg/liter and 133 mg/liter, respectively.	24	7.5	180	49	Cearley and Coleman 1974
90	bluegill *Lepomis macrochirus* juveniles	10% survival after 30 days compared with 60% survival after 60 days at 31 µg Cd/liter. Exposure began with embryos spawned by adults which had been exposed to Cd for 8 to 11 months.	16-26 Seasonal	7.7	207	152	Eaton 1974
110	fathead minnow *Pimephales promelas* adults	Egg production significantly reduced. No significant reduction at 57 µg Cd/liter. Exposure began when fish were 3 weeks old and continued 14 months.	19-25 Seasonal	7.6	204	154	Pickering and Gast 1972.
110	fathead minnow *Pimephales promelas* juveniles	Marked reduction in survival. Survival at 57 µg Cd/liter similar to that in control. Embryos were spawned in Cd solutions by adults which had been exposed to Cd since 3 weeks after hatch. Progeny were exposed for 60 days after hatch. Effect of Cd on parental survival was similar to that observed for progeny.	23	7.6	204	154	Pickering and Gast 1972
850	bluegill *Lepomis macrochirus* juveniles	50% mortality after 138 days. No mortality at 80 µg CD/l. Growth rate of survivors not significantly affected by Cd. Chloride and sulfate concentrations in test water were 193 mg/liter and 133 mg/liter, respectively.	24	7.5	180	49	Cearley and Coleman 1974

Table 17. Toxicity of Lead to Freshwater Crustaceans and Rotifers

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
100	cladoceran *Daphnia magna* adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
280	isopod *Asellus meridianus*	2-day LC50. Test solutions were not renewed; test animals were not fed.	20	NA	25	NA	Brown 1976
300	cladoceran *Daphnia magna* adults	21-day LC50. Pb exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
450	cladoceran *Daphnia magna*	2-day LC50. Pb exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were fed on first day.	18	7.7	45	42	Biesinger and Christenson 1972
600*	cladoceran *Daphnia hyalina* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
4000*	copepod *Eudiaptomus padanus* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
5500*	copepod *Cyclops abyssorum* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
41000*	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974

NOTE: *nominal value

Table 18. Toxicity of Lead to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
3500	mayfly *Ephemerella grandis* nymphs	14-day LC50.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
16000*	mayfly *Ephemerella subvaria* nymphs	50% survival after 7 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
19200	stonefly *Pteronarcys californica* nymphs	Greater than 50% survival after 14 days.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
32000*	caddisfly *Hydropsyche betteni* larvae	50% survival after 7 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
64000*	stonefly *Acroneuria lycorias* nymphs	Greater than 50% survival after 14 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969

NOTE: *nominal value

Table 19. Toxicity of Lead to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
31	rainbow trout *Salmo gairdneri* adults	Spinal curvature occurred in 44% of the fish. 3% had curved spines at 15 µg Pb/liter. Pb exposure began just after swim-up, continued until 19 months after hatch. No spawning occurred in treatments or controls. Pb was measured by flame AAS on non-acidified samples which had settled for several hours.	11	6.7-7.3	28	26	Davies et al. 1976
83	lake trout *Salvelinus namaycush* juveniles	Significant reduction in survival rate. No significant reduction at 48 µg Pb/liter. No reduction in growth at any Pb concentrations permitting survival. Pb exposure began within 1 day after fertilization (51-55 days before hatch), continued another 60 days.	10	7.0-7.3	33	30	Sauter et al. 1976
119 (Total) 84 (Filtered)	brook trout *Salvelinus fontinalis* third-generation juveniles	Significantly reduced mean weight. No significant reduction at 58 µg Pb/liter. Embryos were spawned in Pb solutions by fish which had been exposed to Pb for an entire life cycle, and whose parents had been exposed for 38 weeks. Pb exposure of the third generation continued until 12 weeks after hatch. Application factor = 0.014 - 0.029 based on total levels.	9	6.8-7.6	44	43	Holcombe et al. 1976
120	bluegill *Lepomis macrochirus* juveniles	Significant reduction in survival rate and mean weight. No significant reduction in either parameter at 70 µg Pb/liter. Pb exposure began within 12 hours after fertilization (2 days before hatch), continued 60 days after hatch.	25	6.7-7.2	41	33	Sauter et al. 1976
136	channel catfish *Ictalurus punctatus* juveniles	Significant reduction in survival rate and mean weight. No significant reduction in either parameter at 75 µg Pb/liter. Pb exposure began 2-3 days after fertilization (6-8 days before hatch), continued another 60 days.	22	6.8-7.3	36	34	Sauter et al. 1976

Table 19 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
146	rainbow trout Salmo gairdneri juveniles	Significant reduction in survival rate. No significant reduction at 71 µg Pb/liter. No reduction in growth at any Pb concentrations permitting survival. Pb exposure began within 1 day after fertilization (35-37 days before hatch), continued another 60 days.	10	6.9-7.4	35	30	Sauter et al. 1976
235	brook trout Salvelinus fontinalis embryos	Hatchability markedly reduced (64% vs. 98% in controls). 86% hatchability at 119 µg Pb/liter. Embryos were spawned in Pb solutions by fish which had been exposed to Pb for 38 weeks.	9	6.8-7.6	44	43	Holcombe et al. 1976
235	brook trout Salvelinus fontinalis adults	No spawning because of severe scoliosis. Normal egg production in one replicate at 119 µg Pb/liter and in both replicates at 58 µg/liter. Fish had been exposed to Pb over their entire life cycle. Previous generation had been exposed for 38 weeks. Spawning of first generation was not affected at 474 µg Pb/liter, the highest treatment level.	9-15 Seasonal	6.8-7.6	44	43	Holcombe et al. 1976
253	white sucker Catostomus commersoni juveniles	Significant reduction in mean weight. No significant reduction 119 µg Pb/liter. No survival at 483 µg/liter, poor survival in other concentrations and control. Pb exposure began within 1 day after fertilization (10-13 days before hatch), continued another 60 days.	17	6.7-7.1	38	35	Sauter et al. 1976
672	rainbow trout Salmo gairdneri embryos	Significant reduction in hatchability. No significant reduction at 443 µg Pb/liter. Pb exposure began within 1 day after fertilization (35-37 days before hatch).	10	6.9-7.4	35	30	Sauter et al. 1976

Table 19 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
850 (Total) 41 (free)	rainbow trout Salmo gairdneri adults	Spinal curvature occurred in 60% of the fish. 10% had curved spines at 380 µg total Pb/liter (32 µg free Pb/l). Pb exposure began with 6-gram juveniles, continued 19 months. No spawning occurred in treatments or controls. Total Pb was measured by flame AAS on non-acidified samples which had settled for several hours. Free Pb was measured by pulse polarography.	15	7.6-8.3	353	243	Davies et al. 1976
5580*	fathead minnow Pimephales promelas juveniles	4-day LC50.	25	7.5	20	18	Pickering and Henderson 1966
23800*	bluegill Lepomis macrochirus juveniles	4-day LC50.	25	7.5	20	18	Pickering and Henderson 1966
442000*	bluegill Lepomis macrochirus juveniles	4-day LC50.	25	8.2	360	300	Pickering and Henderson 1966
482000*	fathead minnow Pimephales promelas juveniles	4-day LC50.	25	8.2	360	300	Pickering and Henderson 1966

NOTE: *nominal value

Table 20. Toxicity of Cobalt to Freshwater Crustaceans and Rotifers

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
12	cladoceran *Daphnia magna*	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
21	cladoceran *Daphnia magna*	21-day LC50. Co exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
1110	cladoceran *Daphnia magna*	2-day LC50. Co exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed. Presence of food increased LC50 to 1620 µg Co/liter.	18	7.7	45	42	Biesinger and Christenson 1972
1320 *	cladoceran *Daphnia hyalina* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
4000 *	copepod *Eudiaptomus abyssorum* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
15500 *	copepod *Cyclops abyssorum* adults	2-day LC50. Test solutions were not renewed; test animals were not fed.	10	7.2	33	29	Baudouin and Scoppa 1974
59000 *	rotifer *Philodina acuticornis* mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974

NOTE: *nominal value

Table 21. Toxicity of Cobalt to Aquatic Insects

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
16000*	mayfly *Ephemerella subvaria* nymphs	4-day LC50. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
32000*	caddisfly *Hydropsyche betteni* larvae	50% survival after 7 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969
32000*	stonefly *Acroneuria lycorias* nymphs	50% survival after 8 days. Test solutions were not renewed; test animals were not fed.	18	7.3	44	40	Warnick and Bell 1969

NOTE: *nominal value

Table 22. Toxicity of Cobalt to Freshwater Fish

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
50	carp Cyprinus carpio juveniles	No significant reduction in mean weight after 70-day exposure, although growth rate was initially depressed. Test solutions were renewed daily.	NA	NA	NA	NA	Shabalina 1964
86*	carp Cyprinus carpio juveniles	1-day LC50. Test solutions were not renewed; test fish may or may not have been fed.	21-23	6.8-7.1	25	NA	Tabata 1969

NOTE: *nominal value

Table 23. Toxicity of Silver to Freshwater Animals

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
1	mayfly Ephemerella grandis nymphs	Less than 50% survival after 14 days.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
7	stonefly Pteronarcys californica nymphs	14-day LC50.	3-9	6.3-7.2	30-70	30-70	Nehring 1976
70	bluegill Lepomis macrochirus juveniles	No mortality and no significant reduction in growth rate during 6-month exposure which began with 3-gram fish. Chloride and sulfate concentrations in test water were 193 mg/liter and 133 mg/liter, respectively.	24	7.5	NA	49	Coleman and Cearley 1974
70	largemouth bass Micropterus salmoides juveniles	Complete mortality during 6-month exposure which began with 10-gram fish. No mortality at 7 µg Ag/liter. No significant effects on growth at concentrations permitting survival. Chloride and sulfate concentrations in test water were 193 mg/liter and 133 mg/liter, respectively.	24	7.5	NA	49	Coleman and Cearley 1974
1700*	rotifer Philodina acuticornis mixed ages	4-day EC50 (concentration which immobilized half the test animals). Test solutions were not renewed; test animals were fed.	20	7.4-7.9	25	24	Buikema et al. 1974

NOTE: *nominal value

Table 24. Toxicity of Trivalent Arsenic to Freshwater Animals

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
2300*	bluegill *Lepomis macrochirus* juveniles	Mean weight 42% less than in controls after 16-week exposure. Survival rate at end of exposure was 52% compared to 90% in controls. At 0.7 mg As/liter, growth was normal but survival rate was still depressed. Growth and survival were normal at 0.4 mg/liter. Experiment was conducted in outdoor pools containing soil and rooted plants. Test solutions were not renewed. Toxic effects were mediated at least in part through reductions in food supply. Ammonia nitrogen was 3.3 mg/liter.	16-28 Outdoor pools	7.6	310	286	Gilderhus 1966
10400	brook trout *Salvelinus fontinalis* adults	11-day LC50.	15	7.8	152	168	Cardwell et al. 1976
10500	fathead minnow *Pimephales promelas* juveniles	14-day LC50.	25	7.8	149	166	Cardwell et al. 1976
14800*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed.	12	7.6	310	286	Gilderhus 1966
18000	channel catfish *Ictalurus punctatus* juveniles	4-day LC50.	25	8.0	140	140	Cardwell et al. 1976
18200	bluegill *Lepomis macrochirus* juveniles	14-day LC50.	25	7.8	147	166	Cardwell et al. 1976

Table 24 continued

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
20200*	bluegill Lepomis macrochirus juveniles	4-day LC50. Test solutions were not renewed; test fish were not fed. NOTE: *nominal value	12	7.6	310	286	Gilderhus 1966

Table 25. Toxicity of Pentavalent Arsenic to Freshwater Animals

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
520	cladoceran Daphnia magna adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
1400	cladoceran Daphnia magna adults	21-day LC50. As exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
7400	cladoceran Daphnia magna	2-day LC50. As exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed.	18	7.7	45	42	Biesinger and Christenson 1972
30000	green sunfish Lepomis cyanellus juveniles	22-day LC50.	20	NA	NA	NA	Sorenson 1976

Table 26. Toxicity of Manganese to Freshwater Crustaceans

Concentration (µg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
5200	cladoceran Daphnia magna adults	50% reproductive impairment during 21-day exposure which began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
5700	cladoceran Daphnia magna adults	21-day LC50. Mn exposure began with animals less than 1 day old. Test solutions were renewed weekly; test animals were fed weekly.	18	7.7	45	42	Biesinger and Christenson 1972
9800	cladoceran Daphnia magna	2-day LC50. Mn exposure began with animals less than 1 day old. Test solutions were not renewed; test animals were not fed.	18	7.7	45	42	Biesinger and Christenson 1972

Table 27. Toxicity of Sodium Ethyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
0.01-0.1*	emerald shiner *Notropis atherinoides*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.1-1.0*	cladoceran *Daphnia magna*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.18-1.8*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
1.0*	rainbow trout *Salmo gairdneri* juveniles	100% mortality in 8-day exposure. Test conditions not specified.	10	7.9-8.2	118-125	NA	Webb et al. 1976
10-50*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976
14-16*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	12	8.6	348	203	Fuerstenau 1974
100-200*	algae	50% reduction in photosynthetic rate in 4-day exposure. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974

NOTE: *nominal value

Table 28. Toxicity of Sodium Isopropyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
0.01-0.1*	bluegill *Lepomis macrochirus*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
0.01-0.1*	emerald shiner *Notropis atherinoides*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.1-1.0*	cladoceran *Daphnia magna*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.3*	rainbow trout *Salmo gairderi* juveniles	100% mortality in 3-day exposure.	10	7.9-8.2	118-125	NA	Webb et al. 1976
0.32-5.6*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
10*	catfish	Greater than 50% survival after 4 days. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
10-100*	algae	50% reduction in photosynthetic rate in 4-day exposure. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
10-100*	snail	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
10-100*	tadpole	4-day LC50. Test conditions not specified	NA	NA	NA	NA	Hardie et al. 1974
18-20*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	12	8.6	348	203	Fuerstenau 1974
100-180*	rainbow trout *Salmo gairdneri* fingerlings	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976
		NOTE: *nominal value					

Table 29. Toxicity of Potassium Amyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
0.1-1.0*	cladoceran *Daphnia magna*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
1.0*	rainbow trout *Salmo gairdneri* juveniles	100% mortality in 28-day exposure.	10	7.9-8.2	118-125	NA	Webb et al. 1976
1.0-10*	snails	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
1.8-18*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
10-100*	emerald shiner *Notropis atherinoides*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
32-52*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976
70-80*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions not renewed.	12	8.6	348	203	Fuerstenau 1974
100-200*	algae	50% reduction in photosynthetic rate in 4-day exposure. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974
100-200*	bluegill *Lepomis macrochirus*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hardie et al. 1974

NOTE: *nominal value

Table 30. Toxicity of Potassium Ethyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
0.01-0.1*	emerald shiner *Notropis atherinoides*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.1-1.0*	cladoceran *Daphnia magna*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.1-1.0*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
0.5*	rainbow trout *Salmo gairdneri* juveniles	100% mortality in 2-day exposure.	10	7.9-8.2	118-125	NA	Webb et al. 1976
10-100*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976
15-17*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	12	8.6	348	203	Fuerstenau 1974
15-20*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed. Increasing the test temperature to 20C decreased the 4-day LC50 to 1.5-1.8 mg/l.	12	8.6	348	203	Fuerstenau 1974

NOTE: *nominal value

Table 31. Toxicity of Potassium Hexyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
10-100*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976
100-1000*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972

NOTE: *nominal value

Table 32. Toxicity of Potassium Isopropyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
3.2-32*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
32-320*	rainbow trout *Salmo gairdneri* juveniles	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976

NOTE: *nominal value

Table 33. Toxicity of Sodium Isobutyl Xanthate to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
0.56-10*	cladoceran Daphnia magna	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
10-100*	emerald shiner Notropis atherinoides	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
32-320*	fathead minnow Pimephales promelas	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
56-100*	rainbow trout Salmo gairdneri	4-day LC50. Test solutions were not renewed.	10	7.9-8.2	118-125	NA	Webb et al. 1976

NOTE: *nominal value

Table 34. Toxicity of Sec-butyl Xanthates to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk	Reference
Sodium Sec-butyl Xanthate 0.56-10*	cladoceran *Daphnia magna*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
Potassium Sec-butyl Xanthate 1.0-10*	emerald shiner *Notropis atherinoides*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
Sodium Sec-butyl Xanthate 32-320*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972
Sodium Sec-butyl Xanthate 100-166*	rainbow trout *Salmo gairgneri* Juveniles	4-day LC50. Test solutions were not renewed	10	7.9-8.2	118-125	NA	Webb et al. 1976

NOTE: *nominal value

Table 35. Toxicity of Methyl Isobutyl Carbinol to Freshwater Organisms

Concentration (mg/l)	Species	Effect	°C	pH	Hard (mg/l $CaCO_3$)	Alk (mg/l $CaCO_3$)	Reference
100-1000*	fathead minnow *Pimephales promelas*	4-day LC50. Test conditions not specified.	NA	NA	NA	NA	Hawley 1972

NOTE: *nominal value

Table 36. Toxicity of Hydrogen Ion to Freshwater Invertebrates

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk* (mg/l $CaCO_3$)	Reference
6.6	stonefly Isogenus frontalis nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 3 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
6.35	mayfly Rhithrogena robusta nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
6.18	mayfly Heptagenia sp. nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
6.04	mayfly Cinygmula par nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.90	mayfly Hexagenia limbata nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.8	mayfly Ephemerella grandis nymphs	48-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.8	stonefly Acroneuria pacifica nymphs	90-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.7	mayfly Ephemerella subvaria nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 5 µg/l.	18.5	7.6-7.8	45	40	Bell 1971

Table 36 continued

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk*	Reference
5.7	stonefly Pteronarcys dorsata nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 5 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
5.33	stonefly Arcynopteryx parallela nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.21	mayfly Leptophlebia sp. nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.2	dragonfly Boyeria vinosa nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 7 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
5.2	dragonfly Ophiogomphus rupinsulensis nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 7µg/l.	18.5	7.6-7.8	45	40	Bell 1971
5.15	stonefly Isogenus aestivalis nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
5.13	mayfly Ephemerella doddsi nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973

Table 36 continued

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk*	Reference
5.1	stonefly Acroneuria lycorias nymphs-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 8 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
5.0	midge Tanytarsus dissimilis larvae-pupae-adults	Normal larval survival and pupation, but failure to emerge from pupal case. Normal emergence at pH 5.5. Experiment began with larvae, continued 45 days. Test solutions were not renewed. CO_2 conc. was about 8 µg/l.	18.5	7.8	50	40	Bell 1970
4.95	stonefly Pteronarcys californica nymphs	90-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.7	caddisfly Hydropsyche betteni larvae-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 9 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
4.65	mayfly Ephemerella subvaria nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
4.60	stonefly Pteronarcys californica nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.52	caddisfly Cheumatopsyche sp. larvae	90-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973

Table 36 continued

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk*	Reference
4.52	stonefly Pteronarcella badia nymphs	90-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.37	stonefly Pteronarcella badia nymphs	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.3	caddisfly Brachycentrus occidentalis larvae	90-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.25	stonefly Pteronarcys dorsata nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
4.2	snipe fly Atherix variegata larvae	68-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
4.0	caddisfly Brachycentrus americanus larvae-adults	Emergence rate 50% of that at pH 7.8. CO_2 conc. was about 13 µg/l.	18.5	7.6-7.8	45	40	Bell 1971
3.68	stonefly Isogenus frontalis nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969

Table 36 continued

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk* (mg/l $CaCO_3$)	Reference
3.64	black fly Simulium vittatum larvae	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
3.5	dragonfly Ophiogomphus rupinsulensis nymphs	4-day LC50. CO_2 conc. was not stated	11	7.8	NA	42	Bell and Nebeker 1969
3.34	caddisfly Hydropsyche sp. larvae	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
3.32	mayfly Stenonema rubrum nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
3.32	stonefly Acroneuria lycorias nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
3.31	mayfly Stenonema sp. nymphs	4-day LC50.	11-14	7.1	5	2	Butler et al. 1973
3.25	dragonfly Boyeria vinosa nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
3.25	stonefly Taeniopteryx maura nymphs	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969

Table 36 continued

pH^1	Species	Effect	°C	pH^2	Hard* (mg/l $CaCO_3$)	Alk*	Reference
2.83	caddisfly Limnephilus ornatus larvae	4-day LC50. CO_2 conc. was not stated.	9.5	7.8	135	NA	Gaufin 1973
2.75	stonefly Pteronarcys proteus nymphs	4-day LC50.	11-14	7.1	5	2	Butler et al. 1973
3.16	stonefly Acroneuria lycorias nymphs	4-day LC50.	11-14	7.1	5	2	Butler et al. 1973
3.15	caddisfly Hydropsyche betteni larvae	4-day LC50. CO_2 conc. was not stated.	11	7.8	NA	42	Bell and Nebeker 1969
2.25	dragonfly Boyeria vinosa nymphs	4-day LC50.	11-14	7.1	5	2	Butler et al. 1973
1.72	dobsonfly Nigronia fasciata larvae	4-day LC50.	11-14	7.1	5	2	Butler et al. 1973
1.5	caddisfly Brachycentrus americanus larvae	4-day LC50. CO_2 conc was not stated.	11	7.8	NA	42	Bell and Nebeker 1969

NOTE: pH^1 - Test pH *before acidification
pH^2 - Acclimation pH

Table 37. Toxicity of Hydrogen Ion to Freshwater Fish

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk* (mg/l $CaCO_3$)	Reference
6.1	brook trout Salvelinus fontinalis embryos	Significant reduction in hatchability. No significant reduction at pH 6.6. Author stated that CO_2 conc. was too low to be toxic	12.4	7.0	83	37	Menendez 1976
6.1	brook trout Salvelinus fontinalis juveniles	49% mortality compared with 28% mortality at pH 6.6 and 26% mortality at pH 7.0. Fish had been exposed to low pH since fertilization; parents had been exposed to low pH for 5 months before spawning. Author stated that CO_2 conc. was too low to be toxic	12.4	7.0	83	37	Menendez 1976
5.9	fathead minnow Pimephales promelas embryos	Hatchability significantly reduced. No significant reduction at pH 6.6. Embryos were spawned at low pH by adults which had been exposed to low pH since hatch. CO_2 conc. was not stated	22.3	7.5	201	156	Mount 1973
5.9	fathead minnow Pimephales promelas adults	Egg production significantly reduced. No significant reduction at pH 6.6. Fish had been exposed to low pH since hatch. CO_2 conc. was not stated.	22.3	7.5	201	156	Mount 1973
5.3	white sucker Catostomus commersoni larvae	Significant reduction in survival to swim-up stage. No significant reduction at pH 5.7. Similar effects in harder water. Exposure to low pH began within 2.5 hr. after fertilization. Test solutions were aerated for 24 hr. before use to remove excess CO_2.	17.3-19.2	7.1	93	139	Trojnar 1977a
5.1	brook trout Salvelinus fontinalis adults	Significant reduction in the number of viable eggs produced. No significant reduction at pH 5.6. Exposure to low pH began 5 months before initiation of spawning, continued until 2 weeks after spawning ceased. Author stated that CO_2 conc. was too low to be toxic.	12.4	7.0	83	37	Menendez 1976
4.7	brook trout Salvelinus fontinalis embryos	No significant effect on hatchability. Lower pH levels not tested. Exposure to low pH began immediately after fertilization. Test solutions were aerated for 24 hr. before use to remove excess CO_2.	10	8.0	NA	NA	Trojnar 1977b

Table 37 continued

pH[1]	Species	Effect	°C	pH[2]	Hard* (mg/l $CaCO_3$)	Alk* (mg/l $CaCO_3$)	Reference
4.5	rainbow trout Salmo gairdneri juveniles	50% mortality after 16 days. Test solutions were renewed daily. Fresh solutions had been aerated for 18 hr. before use to remove excess CO_2.	14.5-17.5	NA	320	NA	Lloyd and Jordan 1964
4.5	white sucker Catostomus commersoni embryos	Hatchability significantly reduced. No significant reduction at pH 5.0. Similar effects in harder water. Exposure to low pH began within 2.5 hr. after fertilization. Test solutions were aerated for 24 hr before use to remove excess CO_2.	17.3-19.2	7.1	93	139	Trojnar 1977a
4.2	northern pike Esox lucius larvae	97% mortality after 8-day exposure. 26% mortality after 8 days at pH 5.0. Exposure to low pH probably began within 1 day after hatch. Test solutions were aerated for 3 days before use to remove excess CO_2.	22	NA	34	58	Johansson and Kihlstrom 1975
4.2	white sucker Catostomus commersoni juveniles	50% mortality after 40 days. CO_2 concentration not stated	16	7.6	144	89	Beamish 1972
4.0	brook trout Salvelinus fontinalis larvae	Complete mortality within 14 days after all embryos had hatched. Embryos had been exposed to pH 8.1 from fertilization until all were hatched. When embryos had been exposed to pH 4.7, 40% of larvae died at pH 4.0. Test solutions were aerated for 24 hr before use to remove excess CO_2.	10	8.0	NA	NA	Trojnar 1977b
3.5	brook trout Salvelinus fontinalis juveniles	7-day LC50. Effects were the same at both test temperatures. All fish had been held at 15C before the tests. CO_2 conc. was not stated	10,20	6.8	NA	NA	Daye and Garside 1975

NOTE: pH^1 - Test pH *before acidification
pH^2 - Acclimation pH

Table 38. Percentage increase in 1-day LC50 when hardness is increased from 25 mg/1 to 100 mg/1 as $CaCO_3$ (from Tabata, 1969b).

	Cu	Ni	Zn	Cd	Co	Mn
Daphnia spp.	80	120	140	150	60	30
carp	40	100	80	150	90	10

Table 39. Effect of hardening stream and spring water on the toxicity of copper to the bluntnose minnow (from Geckler et al. 1976).

TEST DATE	DILUTION WATER	HARDNESS (mg/1 as $CaCO_3$)	ALKALINIGY (mg/1 as $CaCO_3$)	pH	2-Day LC50 (µg Cu/1)
8/20/69	stream water	170	150	7.9	570
	modified stream water	234	146	7.9	850
	modified stream water	302	144	7.9	1600
8/21/69	stream water	218	180	8.1	3000
	modified stream water	284	178	8.0	3500
8/25/69	stream water	276	216	8.0	9200
	modified stream water	330	208	7.9	9200
	modified stream water	370	210	8.0	8000
8/29/69	spring water	132	100	7.7	150
	modified spring water	182	99	---	200
	modified spring water	233	99	7.6	180
	modified spring water	282	99	7.6	260
	modified spring water	337	99	7.7	260

Table 40. Copper toxicity of Daphnia magna in Lake Superior water with added bicarbonate (from Andrew et al. 1977).

ADDED ALKALINITY (mg/1 as $CaCO_3$)	TOTAL COPPER (µg/1)	DISSOLVED COPPER (µg/1)	MEDIAN SURVIVAL TIME (min)
none	318	215	∿50
100	318	245	60
200	318	262	73
400	318	268	451
1000	318	278	544

Table 41. Copper and zinc toxicity to juvenile Atlantic salmon in different concentrations of humic acid (from Carson and Carson 1972).

HUMIC ACID CONCENTRATION (mg/l)	4-DAY LC50 (µg Cu/l)	(µg Zn/l)
0	25	740
5	90	740
10	165	740

Table 42. Effects of metal mixtures on fish.

TOXICANTS	SPECIES	EFFECT	TYPE OF JOINT ACTION	TEMPERATURE (C)	pH	HARDNESS (mg/l as $CaCO_3$)	ALKALINITY (mg/l as $CaCO_3$)	REFERENCE
Cu-Ni	guppy	4-day LC50	additive	25	7.0	124	236	Anderson(19
Cu-Ni	guppy	food consumption	more than additive	--	---	---	---	Muska and Weber (197
Cu-Ni	guppy	weight gain	additive or more than additive depending on ration size	--	---	---	---	"
Cu-Ni	guppy	growth efficiency (weight gain/food consumption)	additive	--	---	---	---	"
Cu-Zn	rainbow trout	median lethal time	additive	18	---	320	---	Lloyd(1961b
Cu-Zn	rainbow trout	median lethal time	additive at low concentrations, more than additive at high concentrations	16	---	18	---	"
Cu-Zn	Atlantic salmon	median lethal time	more than additive	17	7.3	20	12	Sprague(196
Cu-Zn	Atlantic salmon	7-day LC50	additive, but more than additive during first day of test	17	7.3	14	--	Sprague and Ramsay(1965
Cu-Zn	guppy	4-day LC50	more than additive(x2.6)	25	7.0	124	236	Anderson(19
Cu-Ni-Zn	rainbow trout	2-day LC50	additive	17	7.4	240	---	Brown and Dalton(1970)

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1	1	10	100	1,000	10,000	100,000
TISSUE ACCUMULATION (EFFECTS UNKNOWN)			AF				
DECREASED EGG LAYING SUCCESS			F	F			
DECREASED HATCHABILITY OF EGGS			F				
DECREASED EGG PRODUCTION			F	F			
DECREASED EMBRYO SURVIVAL			F				
DECREASED WEIGHT / GROWTH RATE		F	ACFIM	A			
DECREASED STANDING CROP / POPULATION		ACF	F				
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)		C	CFM				
LC50 -- 15-25 DAYS			C				
LC50 -- 10-15 DAYS			I	I		I	
LC50 -- 4-10 DAYS			M	FP	FIP		
LC50 -- 1--4 DAYS		C	C	CI	C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 1. Summarization of the levels of copper which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1→→→→→→→→→1→→→→→→→→→→10→→→→→→→→→→100→→→→→→→→→1,000→→→→→→→10,000→→→→→→100,000→→→→						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)		C					
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS							
DECREASED EGG PRODUCTION			C	I			
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE				A			
DECREASED STANDING CROP / POPULATION		A					
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)						I	
LC50 -- 15-25 DAYS				C			
LC50 -- 10-15 DAYS							
LC50 -- 4-10 DAYS					FIP	FIP	
LC50 -- 1--4 DAYS				C	CP	C	

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 2. Summarization of the levels of nickel which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000 →						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)		A			C		
DECREASED EGG LAYING SUCCESS				F	F		
DECREASED HATCHABILITY OF EGGS				F	F		
DECREASED EGG PRODUCTION				C			
DECREASED EMBRYO SURVIVAL					F		
DECREASED WEIGHT / GROWTH RATE				A			
DECREASED STANDING CROP / POPULATION				A			
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)				F	FI	I	
LC50 -- 15-25 DAYS				CF	F		
LC50 -- 10-15 DAYS					F		
LC50 -- 4-10 DAYS				M	FMP		
LC50 -- 1--4 DAYS			C	C	C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 3. Summarization of the levels of zinc which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000 →						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)		C	A				
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS			F				
DECREASED EGG PRODUCTION		CF	F	F			
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE		F	AF				
DECREASED STANDING CROP / POPULATION		CF	F				
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)		F	F	AF		I	
LC50 -- 15-25 DAYS		C					
LC50 -- 10-15 DAYS							
LC50 -- 4-10 DAYS				P	I	I	
LC50 -- 1--4 DAYS			C	C	C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 4. Summarization of the levels of cadmium which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1 →	1 →	10 →	100 →	1,000 →	10,000 →	100,000 →
TISSUE ACCUMULATION (EFFECTS UNKNOWN)		C					
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS				F			
DECREASED EGG PRODUCTION				CF			
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE			F	A			
DECREASED STANDING CROP / POPULATION							
MORPHOLOGICAL DEFECTS			F	F			
DECREASED SURVIVAL (VARYING DEGREES)			F	F		I	
LC50 -- 15-25 DAYS				C			
LC50 -- 10-15 DAYS					I		
LC50 -- 4-10 DAYS					FI	FIP	
LC50 -- 1--4 DAYS				C	C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 5. Summarization of the levels of lead which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l)						
	0.1	1	10	100	1,000	10,000	100,000
TISSUE ACCUMULATION (EFFECTS UNKNOWN)							
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS							
DECREASED EGG PRODUCTION			C				
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE		F		A			
DECREASED STANDING CROP / POPULATION							
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)						I	
LC50 -- 15-25 DAYS			C				
LC50 -- 10-15 DAYS							
LC50 -- 4-10 DAYS						IP	
LC50 -- 1--4 DAYS			F		C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 6. Summarization of the levels of cobalt which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l) 0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000 →
TISSUE ACCUMULATION (EFFECTS UNKNOWN)	F
DECREASED EGG LAYING SUCCESS	
DECREASED HATCHABILITY OF EGGS	
DECREASED EGG PRODUCTION	
DECREASED EMBRYO SURVIVAL	
DECREASED WEIGHT / GROWTH RATE	A A
DECREASED STANDING CROP / POPULATION	
MORPHOLOGICAL DEFECTS	
DECREASED SURVIVAL (VARYING DEGREES)	I F
LC50 -- 15-25 DAYS	
LC50 -- 10-15 DAYS	I
LC50 -- 4-10 DAYS	
LC50 -- 1--4 DAYS	P

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 7. Summarization of the levels of silver which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l) 0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)						C	
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS							
DECREASED EGG PRODUCTION				C			
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE					F		
DECREASED STANDING CROP / POPULATION							
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)					F		
LC50 -- 15-25 DAYS						F	
LC50 -- 10-15 DAYS						F	
LC50 -- 4-10 DAYS						F	
LC50 -- 1--4 DAYS					C		

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 8. Summarization of the levels of arsenic which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l) 0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000 →						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)							
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS							
DECREASED EGG PRODUCTION							
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE							
DECREASED STANDING CROP / POPULATION							
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)					F	F	F
LC50 -- 15-25 DAYS							
LC50 -- 10-15 DAYS							
LC50 -- 4-10 DAYS					CF	CFM	M
LC50 -- 1--4 DAYS							

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 9. Summarization of the levels of xanthates which affect aquatic organisms.

STRESS EFFECTS	CONCENTRATION (µg/l) 0.1 → 1 → 10 → 100 → 1,000 → 10,000 → 100,000						
TISSUE ACCUMULATION (EFFECTS UNKNOWN)							
DECREASED EGG LAYING SUCCESS							
DECREASED HATCHABILITY OF EGGS							
DECREASED EGG PRODUCTION							
DECREASED EMBRYO SURVIVAL							
DECREASED WEIGHT / GROWTH RATE							
DECREASED STANDING CROP / POPULATION							
MORPHOLOGICAL DEFECTS							
DECREASED SURVIVAL (VARYING DEGREES)							
LC50 -- 15-25 DAYS							
LC50 -- 10-15 DAYS							
LC50 -- 4-10 DAYS				F			
LC50 -- 1--4 DAYS							

A- ALGAE C- CRUSTACEANS F- FISH I- INSECTS M- MOLLUSCS P- PROTOZOANS

LITERATURE DATA INDICATE EFFECTS IN THIS ORDER OF MAGNITUDE

INDICATES NO LITERATURE DATA AND/OR EFFECTS IN THIS ORDER OF MAGNITUDE

FIGURE 10. Summarization of the levels of carbinol which affect aquatic organisms.

FIGURE 11. Summary of the effects of pH on aquatic organisms.