HEAVY METAL ACCUMULATION IN AQUATIC ORGANISMS

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Regional Copper-Nickel Study:

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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.

ABSTRACT

Interpretation of measured concentrations of heavy metals in aquatic organisms requires an understanding of the mechanisms of accumulation. Literature concerning the processes of uptake, storage and excretion of heavy metals and the factors which influence these processes is reviewed, and reported concentrations of several metals in organisms from polluted and unpolluted locations are summarized. Metal concentrations in aquatic macrophytes, bivalve molluscs and fish from the Regional Copper-Nickel Study Area are found to be within previously reported ranges.

Experimental studies and field surveys which included organisms from several trophic levels are reviewed and the compartmentalization and fate of heavy metals in aquatic ecosystems is discussed. Although the food chain may serve as a source of heavy metals to aquatic organisms, there is no concrete evidence of magnification through the food chain of the elements considered in this review.

The use of aquatic organisms to monitor heavy metal pollution is reviewed. Of the groups studied, it appears that some aquatic macrophytes and bivalve molluscs are best suited to this task, although several problems involved in the interpretation of measured tissue concentrations exist. Data collected by the Regional Copper-Nickel Study indicate that leaves of *Nuphar variegatum* may adequately reflect levels of copper and nickel in the sediments and water, and may be suitable as monitors of pollution by these metals.

INTRODUCTION

The release of heavy metals into the aquatic environment may cause direct effects on the indigenous organisms such as reduced reproductive success, growth or survival. These effects lead to alterations in the structure and function of aquatic ecosystems. Further, less direct effects may occur as aquatic organisms accumulate heavy metals and potentially transfer these metals through the food chain. These accumulated metals may act as toxins, if the levels in tissues become high enough.

The development of the copper-nickel resource in northeastern Minnesota may result in increased heavy metal concentrations in the lakes and streams of the region. In order to determine what biological effects heavy metals might have on these aquatic ecosystems, several studies were initiated as part of the Regional Copper-Nickel Study. The direct toxicity of heavy metals to aquatic organisms was studied in field and laboratory tests and through a review of literature. Similarly, the accumulation and biological pathways of heavy metals was investigated through field surveys in the Regional Copper-Nickel Study Area (Study Area) and through a review of the available literature.

This report presents the information on accumulation and biological pathways of heavy metals while the toxicity of heavy metals is dealt with in a separate report. The first portion of this report reviews the literature which deals with the accumulation of nine heavy metals (Cu, Ni, Zn, Cd, Co, Ar, Pb, Ag, Mn)by aquatic organisms, the biological pathways of these heavy metals in aquatic ecosystems, and the potential use of aquatic organisms as biomonitors. The second portion of the report presents the results of the field surveys of 1976 and 1977. This survey was conducted to determine the levels of heavy metals in various trophic levels of the aquatic ecosystems in the Study Area and the relationship between these levels and the levels in water and sediments.

ACCUMULATION OF HEAVY METALS BY AQUATIC ORGANISMS

Heavy metals are accumulated to some extent from the environment by all aquatic organisms. Some metals, such as zinc, are essential to certain metabolic processes and are necessary in small quantities, although they are toxic at higher concentrations. Others, such as lead and cadmium, serve no known physiological function, and cause toxic responses even at low concentrations.

The amount of an element that is accumulated by an organism depends on several factors, some of which are related to environmental parameters, and others which depend on the way an organism deals with the element. Among the first group, the sources from which an organism can obtain heavy metals, and factors that influence the availability of the metals are considered. In general terms, organisms can accumulate metals from water, sediments and ingested food. The relative contribution of each of these sources has received little attention. Further, the form of a metal will influence its availability for uptake and accumulation. Several water quality parameters, such as pH and TOC, alter the form of metals and various authors (Windom and Smith 1973, Karbe and Schnier 1975, Merlini and Pozzi 1977a) have reported effects on metal uptake related to these parameters. Metals contained in ingested food may be firmly bound and unavailable for uptake (Bryan 1976). For example, although zebrafish, Brachydanio rerio were given food that contained cadmium at concentrations that would have been acutely lethal to the fish .

had the metal been in the water, relatively low quantities were accumulated and toxic effects were not observed (Rehwoldt and Karimian-Teherani 1976). The question of the assimilation efficiency for metals in different forms has received little attention in the literature.

The quantity of a metal accumulated also depends on the extent to which an organism can control the processes of uptake, storage and excretion of the metal. The efficiency of regulation varies for different metals and different organisms. For example, fish and decapod crustaceans appear to be able to regulate the uptake of essential metals, such as copper and zinc, until a certain concentration is exceeded. However. non-essential elements, such as lead, are not regulated. The situation is quite different for bivalve mollusks, which apparently are unable to regulate the accumulation of any metal.

It is necessary to understand the processes of uptake, storage and loss and the factors that affect these processes in order to properly interpret measured concentrations of metals in aquatic organisms. This section is a review of the literature concerned with these processes.

Reported concentrations of heavy metals in aquatic organisms have been compiled into Figures 1 through 47. The concentration of each metal for each general group of organisms has been placed on a separate figure. These figures provide a means to compare species differences within groups and differences between groups.

Bacteria

Although little information is available, it is apparent that bacteria play an important role in trace metal cycling in aquatic ecosystems. Several heavy metals are accumulated by bacteria, which are then available for transport through the food chain. Bacteria also participate in the precipitation of metals and can convert some metals (lead and arsenic) from an inorganic to an organic state.

Copper - Bacteria can accumulate copper, which is then available for food chain transfer.

In a mixed culture of eleven species of bacteria isolated from freshwater sediments, bacterial accumulation of copper increased with increasing concentration of added copper (Patrick and Loutit 1976). The increase was slight at 1000 μg Cu/l but levels were four times those of controls at 2000 μg/l. Five other metals were added simultaneously, so interpretation is difficult. It is likely that much of the added copper was rapidly precipitated and/or that these bacteria were tolerant, as no effects on bacterial growth were observed.

Tubificid worms fed these bacteria accumulated more copper than those fed unexposed bacteria, indicating that accumulated copper was available for transport through the food chain. However, no evidence of biomagnification was noted.

Cadmium - Bacteria can accumulate and precipitate cadmium. Mixed cultures from Corpus Christi Harbor removed 70% of added ^{109}Cd from solution in 120 hours (McLerran and Holmes 1974). Approximately 10-15% of this cadmium was associated with the bacteria. The rest was precipitated, probably as CdS or as a coprecipitate of iron. Cadmium removal curves paralleled bacterial growth curves and field observations indicated that periods of maximum CdS deposition corresponded to times of maximum bacterial activity. It is clear that bacteria play an important role in cadmium cycling in this system.

CdS precipitation has also been described in freshwater systems, under anaerobic conditions. It is possible that under reducing conditions adsorbed cadmium could be released from bacteria to the sediments as precipitate (Yost and Atchinson 1975).

Zinc - Bacteria accumulate zinc from water and may also cause deposition of zinc in the sediments. Accumulated zinc is available for transport in the food chain.

Mixed cultures from Corpus Christi Harbor removed 85% of added ^{65}Zn from solution in 120 hours. Twenty percent of this zinc was associated with the bacteria, while 80% was precipitated, probably as ZnS or as a coprecipitate of FeS. Curves for zinc removal paralleled bacterial growth curves; field observations indicated that maximum bacterial activity and H_2S production coincided with maximum zinc deposition (McLerran and Holmes 1974). Mixed cultures of eleven species of bacteria isolated from freshwater sediments accumulated zinc to nearly twice control levels when either 1000 or 2000 μg Zn/l were added to test solutions. (Patrick and Loutit 1976). Zinc uptake may have been regulated, or much of the added zinc may have precipitated. Tubificids fed these bacteria accumulated more zinc than worms fed unexposed bacteria, indicating that accumulated zinc was available for transport through the food chain.

Lead - Bacteria can accumulate lead and pass it through the food chain. There is some evidence that the form of lead may be altered by bacteria.

Mixed cultures of eleven species of bacteria isolated from freshwater sediments accumulated lead to about eight times control levels when exposed to 1000 μg Pb/l and about nine times control levels when this concentration was doubled (Patrick and Loutit 1976). This may indicate regulation of lead uptake at high concentrations but is more probably the result of saturation of binding sites. Tubificid worms fed on exposed bacteria had higher levels of lead than worms fed on unexposed bacteria, indicating that this lead was available for transfer in the food chain. Most of the lead accumulated by cultures of Micrococcus luteus and Axotobacter sp. was found in the cell wall and membrane fractions (Tornabene and Edwards 1972).

One would predict that lead ion would not be methylated (Wood 1973). However, Wong et al. (1975) have shown that methylation of Me_3Pb salts to Me_4Pb occurs in lake water and nutrient medium, and that conversion of inorganic lead salts (nitrate and chloride) to Me_4Pb can occur in certain sediments. Several bacterial genera were implicated.

Arsenic- Arsenic can be reduced and methylated in sediments to di- and trimethylarsine, both of which are toxic and volatile. These are generally oxidized to produce less toxic products. However, they may be intermediated in the synthesis of dimethylarsine from arsenic salts. Alkyl arsenic compounds have been shown to accumulate in shellfish in Norway (Wood 1973).

Manganese - Manganese is accumulated by bacteria and can be passed through the food chain. In mixed cultures of eleven species of bacteria isolated from freshwater sediments accumulated approximately twelve times control levels when 1000 µg Mn/l were added to solution and nearly forty-five times control levels when 2000 µg Mn/l were added (Patrick and Loutit 1976). Accumulated manganese was shown to be transferred to tubificids fed on these bacteria. No indication of biomagnification was noted.

Algae

The accumulation of metals by algae appears to be a passive process, although there may be some metabolic control over uptake of essential elements such as zinc. While it is possible that algae can be used to monitor metal levels in the environment, several problems are obvious. Collection of unialgal samples is difficult, and different groups of species are present at different times of the year. A better approach was suggested by Wood (1975). Unialgal cultures would be maintained in the laboratory. Samples of these cultures in plastic bags would be placed in the water, and the metal concentrations in the algae measured at intervals. The resulting data on uptake rates would give an indication of the level of pollution in the water.

Copper - The uptake of copper by algae is rapid. For example, the marine algae, Gonyaulux tamarensis, removed up to 25% of available copper, some of which was released back to the medium. (Morel and Morel 1977). Equilibrium occurred in ten to fifteen minutes. Proportionately less copper was removed at higher concentrations. Uptake is apparently a passive process, not requiring the expenditure of metabolic energy. Rana and

Kumar (1974) found that uptake was independent of growth in Chlorella vulgaris and Anacystis nidulans.

Copper may or may not penetrate algal cells. Photosynthesis was inhibited in Nitzschia palea when copper was observed within the cell. In contrast, division and growth of Chlorella pyrenoidosa were inhibited although copper did not penetrate the cells (Steemann-Nielsen and Wium-Anderson 1970).

In those species in which copper penetrates the cells, accumulation seems to be proportional to the concentration of copper in the medium. This has been observed for marine (Bentley-Mowat and Reid 1977) and freshwater algae (Stokes et al. 1973). The latter authors found that uptake by Scenedesmus acuminatus was linear with respect to ambient concentration and exposure time when cells were in the exponential phase.

Copper-tolerant strains of Chlorella and Scenedesmus have developed in certain lakes of the Sudbury region. Stokes et al. (1973) have found that tolerant strains of Scenedesmus accumulate more copper than non-tolerant forms. Similar results have been obtained by Bentley-Mowat and Reid (1977) using two species of marine algae.

While this phenomenon may occur in some cases, it is incorrect to think that it may be generally applicable. Gibson (1972) found that Scenedesmus quadricula, which is more resistant to copper pollution than Anabeana flos-aquae, accumulated less copper at similar ambient concentrations. Cells of both species died when copper concentrations in cells reached about one per cent. These findings indicate that there may be more than one mode of copper toxicity and/or that species differ in the ability to detoxify copper.

Cadmium - Marine algae adsorb cadmium rapidly from the water. Some desorption by external metabolites may occur (Cossa 1976). Absorption probably follows at a slower rate. Mitochondrial cadmium inclusions have been observed (Silverberg 1976).

Zinc - Uptake of ^{65}Zn from water is best described by power functions, and is directly related to ambient concentrations. Whether the process involves adsorption or absorption is not clear and it is likely that both processes are involved (Cushing et al. 1975). These authors suggest that adsorption is more important, because of the direct relationship of algal zinc concentrations to ambient concentrations and evidence which indicated direct cation (e.g. Mg^{+2}) competition at adsorption sites. However, they also note that benthic marine algae accumulate zinc in proportion to net oxygen production, which suggests that zinc is absorbed metabolically. Chipman et al. (1958) observed that little ^{65}Zn leaves Nitzschia closterium cells placed in clean water, which suggests that it is firmly bound.

Lead - Uptake of lead by algal cells is initially rapid, but levels off in minutes, following Freundlich adsorption kinetics. Entry into cells follows later (Schultz-Baldes and Lewin 1976). Uptake is somewhat related to ambient water concentrations. Wood (1975) has also suggested that sediment concentrations may be important.

Aquatic Macrophytes

The mechanisms and dynamics of heavy metal uptake in aquatic macrophytes are poorly understood as few experimental studies have been attempted. There appear to be at least 2 systems of ion uptake that operate in macrophytes. At low external concentrations, a high-affinity system predominates, while at higher concentrations, a low-affinity system operates. At some threshold then, accumulation should level off (Hutchinson 1975). These systems may or may not apply to heavy metal uptake. McLean and Jones (1975) noted that relatively less zinc was absorbed by plants at low ambient concentrations than at high concentrations. The work of Cearly and Coleman (1973) suggests that if ambient levels (of cadmium) are increased sufficiently, toxic reactions may cause a cessation of uptake. On the other hand, Hutchinson and Czyrska (1975) found that at copper concentrations of about 0.1 mg/l, the metal flooded into the cells, resulting in mortality.

Several factors influence metal accumulation in macrophytes:

a) Concentration of the metal in water - Several studies have indicated that there is a direct relationship between water concentration of a particular metal and the concentrations observed in macrophytes (e.g. Mathis 1973, Cowgill 1974). The relationship, however, may not be strictly proportional, and other studies have not found such correlations. Further, at higher concentrations, toxic effects may inhibit uptake (Cearly and Coleman 1973).

b) Concentration of the metal in sediments - The findings of Cowgill (1974) that as much copper, nickel and other metals were accumulated by some non-rooted plants as rooted plants may suggest that sediment levels are not important in determining the concentrations of metals found in macrophytes. However, several studies have indicated that plant tissue burdens are related to sediment concentrations. Small and Gaynor (1975) found higher levels of twelve elements in rooted plants grown on sewage sludge than in plants grown on other substrates. Hutchinson et al. (1975) found correlations between the concentration of nickel in sediments and foliage and copper in sediments and roots of *Typha latifolia*. It has been demonstrated that sediments do release metals to plants regardless of ambient water concentrations (Kniep et al. 1974, Cowgill 1974, Hutchinson et al. 1977).

c) *Availability for uptake* - It is evident that the pattern of distribution of metals in aquatic systems will affect the availability and manner of uptake. For example, it seems that copper is more firmly bound to sediments than nickel (Hutchinson et al. 1975, Fitchko et al. 1976). The opportunity for uptake of sediment-bound metals by rooted plants would be greater than for non-rooted species. Hutchinson et al. (1977) observed an excellent correlation between copper in sediments and roots of *Typha latifolia* but not foliage. Nickel was more evenly distributed through the plant.

d) *Metal translocation within plants* - The differences observed in the preceding section may be the result of differential translocation of elements within a plant. Several studies have shown that various elements are concentrated in different plant parts (Cowgill 1974, Hutchinson et al.1975, Lee et al. 1976). Further, Lee et al. (1976) demonstrated that translocation and the resultant tissue distribution of a given element may vary from species to species. Their general conclusion was that essential micronutrients such as zinc and nickel are translocated from the roots, whereas non-essential elements such as cadmium and lead are not. Uptake of essential elements may be better regulated than uptake of non-essential or toxic elements. Interspecific variation in regulatory ability may also be expected.

e) Physiological factors - Metal accumulation is affected by growth rates and physiological condition (McIntosh 1975, Cowgill 1974). Environmental factors which affect physiological processes, such as seasonal changes, light and pH may also be involved (see McLean and Jones 1975, and Hutchinson 1975 for references).

f) Associated organisms - Epiphytic (Patrick and Loutit 1977) and epifaunal (Ljungren 1971) populations can contribute significantly to concentrations measured in plant tissues if plants are not washed properly. Such populations are species specific which may lead to erroneous conclusions regarding metal burdens in plants.

g) Species differences - It should suffice to note that great interspecific variability of metal burdens has been encountered in the literature. Reference has been made to several areas where these differences may be important. Frequently, variability within a species is also large.

Zooplankton

Direct adsorption of heavy metals from water is probably important in determining the body burdens of zooplankton, as elements are accumulated by the exoskeleton (Martin 1971). Molted zooplankton exoskeletons constitute an important mode of transport of trace elements to the sediments (Fowler and Small 1967, Bertine and Goldberg 1972). Food can be an important source of trace elements in some species. Benayoun et al. (1974) found that food was the most important source of cadmium in the euphausiid, Meganyctiphanes norvegica, with 84% of the total cadmium flux through the organism being accounted for in fecal pellets.

Molluscs

Several sources of heavy metals are available for uptake by molluscs soluble ionic and organic forms, suspended particulate matter, sedimentary deposits and the food web (phytoplankton and detritus). These elements can be adsorbed to free surfaces, absorbed, either actively or passively, and ingested. Little effort has been made to delimit the contribution of each; most experiments have utilized metal ions in water as the only source. Various authors (Frazier 1976, Ayling 1974) have suggested that the sediments represent a more important source of metals; Pentreath (1973) felt that food was a more important source than water. Since most experimental studies have neglected these sources, rates and equilibrium levels measured are not reported. It would be difficult to extend these results to natural conditions, or from one area to another. Further,several investigators have noted anomalies in the uptake of various metals (Harrison 1969, Scott and Major 1972, Brooks and Rumsby 1967).

Molluscs do not effectively regulate the accumulation of metals. Absorption is probably a largely passive process, and excretory mechanisms appear to be poorly developed. There seems to be an upper limit to the amount of metal which can be excreted by the animal. If exceeded, the concentration increases with size or age. The magnitude of differences between the metal concentrations in molluscs from contaminated and uncontaminated areas tends to confirm this (Bryan 1976). These facts, and the generally sedentary nature of the group, have led several authors to propose their use as water quality monitors.

One of the major difficulties in assessing the meaning of trace metal body burdens in molluscs is the great variability encountered between and within species. Levels in animals from the same locations may differ by two orders of magnitude and variation of up to 300% has been observed. Coefficients of variations of 50% are common.

Aside from inherent individual differences, size and sex of the organisms, physiological condition, and variable silt burdens contribute to the variability observed within populations. Other factors, which make comparison of studies difficult are: species differences, season, temperature, salinity, and chemical factors that may affect the availability of the metal to the organisms such as pH, hardness, the presence of other ions, and organic materials that may complex with metals.

Aside from the possible use of molluscs as monitors of water pollution (see pages 63-68), little practical information can be gained from knowledge of body burdens. Only two references were reviewed which attempted to relate body burdens to other phenomena. Roosenberg (1969) found that the degree of greening of oyster tissue was related to tissue copper concentrations.

Increases in coloring were observed when tissue levels reached 0.5 mg Cu/g. Hueck (1975) attempted to relate tissue copper concentrations to LC_{50} values obtained in bioassay experiments. However, Scott and Major (1972) observed continued copper accumulation with no apparent ill effects at concentrations which had resulted in 55% mortality in other tests.

Copper

Uptake - Experimental studies indicate that the rate of copper uptake increases, and then decreases with increasing concentration in the test water. According to Majori and Petronio (1973) the equilibrium concentration reached in mollusc tissue is dependent on the concentration in the water, with concentration factors decreasing with increasing concentration. Decreases in uptake observed at higher concentrations are probably the result of toxic reactions (Pringle et al. 1968). Physiological distress, which depends on the concentration of copper ion and not on the amount of copper accumulated, has been shown to reduce copper uptake in the gastropod *Taphius glabratus* (Yager and Harry 1964). Scott and Major (1972) observed shell closure in *Mytilus edulis* when exposed to high copper concentrations. Therefore, it is possible that large quantities may be accumulated, if accumulated slowly, such that detoxification by binding is not hindered (Scott and Major 1972).

Field studies using transplanted oysters indicate that sediment concentrations may be more closely related to copper body burdens in burrowing molluscs than water levels. (Frazier 1976).

Localization in tissues - Highest concentrations of copper are found in the digestive gland and kidneys of freshwater and marine bivalves (Seatle and Ehlmann 1974, Pentreath 1973, Bryan 1973). Gill and gonads accumulate moderate amounts; the mantle and muscle tissue accumulate less (Bryan 1973, Pentreath 1973a).

Pentreath (1973a) observed that M. edulis accumulated significant quantities of labeled copper in forty-two days. However, the experiments were relatively short term and redistribution of the nuclide to other organs probably had not occurred.

Excretion - The depuration of copper from molluscs generally proceeds at a slower rate than accumulation. The rate is affected by the exposure, concentration and duration of exposure (Majori and Petronio 1973). High copper concentrations have been observed in granules in the kidneys, which suggests that copper is transported to this organ for detoxification (Bryan 1973). The digestive gland probably also serves this function (Belzer and Pilson 1975). Copper is probably bound in a nontoxic form, since tissue concentrations greater than those attained in organisms exposed to lethal copper concentrations have been observed, without apparent ill effects.

Factors Affecting Uptake

a. Species differences - Several investigators have reported higher levels of copper in oysters than in clams, scallops and mussels (Brooks and Rumsby 1965). These authors found similar levels in scallops and mussels, but Bryan (1973) found marked differences between two species of scallop.

b) Size and Weight - Field studies have revealed poor or no correlation between copper concentration and weight in the oyster Crassostrea virginica

(Hugget et al. 1973) and the freshwater bivalves *Amblema perplicata* and *Anodonta grandis* (Seagle and Ehlmann 1974). Marks (1938) found the relationship to be variable, sometimes being positive, sometimes negative and sometimes copper concentrations were independent of weight.

However, laboratory and transplant studies have shown that, in general, smaller bivalves accumulate copper faster and to higher concentrations than larger animals. For example, Bowden (1974) found copper accumulation in six species of marine bivalves to be related to the 0.75 power of body weight, suggesting a connection with metabolic activities associated with surface area to volume relationships. Small freshwater mussels (*Quadrula quadrula*) transplanted to a polluted stream accumulated more copper than larger animals (Foster 1974). The discrepancy between laboratory results and field observations are likely the result of fluctuations in environmental conditions and high variability in the latter cases.

c) pH - Foster (1974) found that *Quadrula quadrula* accumulated more copper at low (6.9) than high (8.3) pH.

d) Season - Concentrations of copper in the whole soft parts of *Mercenaria mercenaria* and *Crassostrea virginica* achieved maximum levels in summer or early autumn (Roosenberg 1969, Frazier 1975, Romeril 1974). Frazier (1975) found that seasonal changes in copper content was correlated with gonadal development and spawning. Romeril (1974) noted decreased concentrations immediately after spawning. Roosenberg (1969) felt that changes in the copper burden of whole soft parts were related to seasonal changes in body weight which result from changes in the gonadal and storage tissues. These tissues do not participate in copper accumulation to the same extent as other tissues.

In contrast, Bryan (1973) observed the highest levels of copper in two scallop species in January and February. Changes were noted in tissues other than the gonads. He reasoned that summer lows were caused by high primary productivity which decreased the availability of copper by decreasing the amount present in the water as well as the concentration per algal cell. Therefore, assuming a constant feeding rate, less copper would be accumulated by the molluscs.

e) Exposure of parents - According to Grieg et al. (1975), copper levels in oyster (*C. virginica*) eggs do not appear to be dependent on levels found in adults.

Nickel

Uptake - Uptake of nickel by *Mytilus edulis* increased with increasing concentration in the experimental water (Friedrich and Fillice 1976). Equilibrium was reached in five days at the highest concentration tested (0.107 mg/l), but not at lower concentrations. Minimum levels attained increased with increasing concentration in the water, but concentration factors decreased with increasing concentration.

Localization in tissues - The greatest concentration of nickel in two species of scallops was found in the kidneys and digestive glands. Gills, gonads and mantle tissue contained somewhat less nickel, while the lowest concentrations were found in muscular tissue (Bryan 1973).

Other factors affecting uptake

a) Species - Segar et al. (1971) found large differences in nickel concentrations in eleven species of marine molluscs, and Bryan (1973) found differences in the composition of two species of scallop. However, Pringle et al. (1963) reported similar tissue levels in several species of clams and oysters.

b) Weight - Boyden (1974) found a direct (power of 1) relationship of body weight to nickel content in six species of molluscs.

c) Season - Bryan (1973) found higher nickel levels in scallops in autumn and winter and related this to low primary productivity during that period (see Molluscs-Copper for further explanation).

Cadmium

Uptake - Uptake of cadmium is proportional to water concentration and decreases with time. Equilibrium concentrations measured by Marjori and Petronio (1973) were proportional to the exposure level (up to 52 μgCd/l According to Eisler et al. (1972) concentration factors decrease with increasing concentration in the water.

The accumulation of cadmium is rapid. *Crassostrea virginica* were exposed to 10 μgCd/l, a "safe" concentration, for twenty-one days in a flow-through apparatus (Eisler et al. 1972). Body burdens at the end of the experiment were 52.1 mg Cd/kg ash weight while control levels were approximately 3 mg/kg. The amounts accumulated by exposed animals greatly exceeded the emetic threshold of cadmium, 13-15 ppm. It is likely that high body burdens such as these may be achieved over longer periods of time when bivalves are exposed to lower concentrations. *C. virginica* exposed to 5 μgCd/l accumulated up to 10.75 μgCd/g wet weight in forty weeks and equilibrium had not yet been attained (Zaroogian and Cheer 1976).

This phenomenon is probably explained by the fact that cadmium can replace zinc (Graham 1972), which accumulates to high levels in bivalves, and especially in oysters, and is firmly bound to proteins (Brooks and Rumsby 1967).

Localization in tissues - Brooks and Rumsby (1965) found more cadmium in the kidney and digestive gland of two species of scallops, than in the remaining soft parts combined. However, in uptake studies, using the same species, they observed the highest concentrations in the gills, followed by the heart, visceral mass and mantle.

The distribution of cadmium in freshwater bivalves appears to differ from that of marine organisms. Segar et al. (1971) found the highest levels of cadmium in the calcareous tissue of *Anodonta sp.*, a tissue not present in marine bivalves. Further, the body burden of cadmium in this species was higher than in eleven marine species investigated. An examination of the data on *Modiolus modiolus* presented by Segar et al. (1971) confirms the suggestion that the tissue distribution of cadmium resembles that of zinc.

Excretion - The depuration of cadmium is slower than accumulation and the rate of depuration is determined by the duration and intensity of exposure (Majori and Petronio 1973).

Other factors affecting uptake

a) Species - Several studies have noted differences in the body burdens of different species collected from similar locations. For example, Bryan

(1973) found higher levels in *Pecten maximus* than in *Chlamys opercularis*; Brooks and Rumsby (1965) found more cadmium in oysters than in scallops while levels in mussels were undetectable, a finding which is in agreement with that of Talbot et al. (1976). Segar et al. (1971) presented concentrations in eleven species of marine molluscs.

b) *Size and Weight* - Boyden (1974) found a direct relationship between body weight and cadmium concentration in *Mytilus edulis*. However, in *Patella vulgata*, the cadmium concentration was related to the square of body weight, being greater in larger individuals. Ayling (1974) also observed higher concentrations in larger individuals. It may be surmised that this type of relationship would hold for a non-essential element if excretory mechanisms were not well developed. Current data indicate that cadmium is strongly bound to proteins and excretion is slow.

c) *Season* - Zaroogian and Cheer (1976) reported higher levels of cadmium in *Cradsostrea virginica* during the summer than in the winter. This is probably related to increased metabolism and feeding, as no relationship to gonadal development or shell growth was detected in this species by Frazier (1976).

d) *Physiological condition* - Reduced cadmium uptake was observed in distressed snails by Yager and Harry (1964). Distress depends on the concentration of the ion in the environment and not necessarily on the amount accumulated.

e) *Temperature, salinity and other ions* - Jackim et al. (1977) found that increases in temperature increased cadmium uptake by Mytilus edulis in the summer but not in winter. A decrease in salinity was found to increase cadmium uptake; zinc at concentrations of 500 μg/l reduced cadmium rate.

f) Exposure of parents- Cadmium levels in oyster (C. virginica) eggs do not appear to be dependent on the levels found in adults (Grieg et al. 1975).

Zinc

Uptake - Most of the work on zinc uptake has utilized the isotope ^{65} Zn. Although direct comparison of uptake of isotopes and stable elements is difficult, it appears that, in general, the patterns are similar. ^{65}Zinc uptake is characterized by an initial, rapid increase, which may be linear, followed by a leveling off in time (Pauley and Nakatani 1968, Harrison 1969). Equilibrium may be slowly achieved (Keckes et al.1968). Both the rate of uptake and the body burdens achieved increase with increasing concentration of zinc in the water (Harrison 1969). In natural stream conditions, fluctuations in the ^{65}Zn concentration in Lampsilis radiata reflected fluctuations in water concentrations (Harvey 1964). Concentration factors for the radionuclide decrease with increasing water concentrations.

The uptake of stable zinc is similar, with higher body burdens being obtained in animals from water with higher zinc concentrations. Concentration factors decrease with increasing water concentrations (Wolfe 1970). The uptake processes in freshwater and marine organisms are similar, although concentration factors are generally higher in freshwater animals.

Localization in tissues - The results of field and experimental studies measuring stable or isotopic zinc indicate similar tissue distributions for both freshwater and marine species. In general, exposed tissues, such as gills, labial palps and mantle have the highest concentrations of zinc. Internal organs, including the stomach, digestive gland and kidney contain moderate amounts of zinc, while muscle tissue has the lowest levels of this metal (Chipman et al. 1958, Pauley and Nakatani 1968, Harrison 1969, Wolfe 1970). Freshwater bivalves concentrate zinc to the highest degree in the calcareous tissue, where it may be exchanged for calcium ion. This tissue is not present in marine bivalves (Harrison 1969).

Some exceptions to this pattern have been observed. For example, in the scallop, Chlamys opercularis, the highest concentration of zinc was found in the kidney; in Pecten maximus, the highest concentrations were found in the digestive gland and muscular tissue, while gill and mantle tissues contained the lowest concentrations (Bryan 1973).

Excretion - Loss of zinc from organisms placed in "clean" water is slower than the rate of uptake and depends on the duration of exposure and exposure concentration (Keckes et al. 1968). The existence of zinc pools bound to different degrees is indicated (Harrison 1969).

Other factors affecting uptake

a) Species - Oysters accumulate more zinc than clams (Pringle et al. 1968) mussels (Nielsen and Nathan 1975, Brooks and Rumsby 1965), and scallops (Brooks and Rumsby 1965). Bryan (1973) observed differences for two species of scallop taken from the same location.

b) Size and Weight - Harrison (1969) found that uptake of zinc was inversely related to weight in freshwater bivalves. Similarly, smaller oysters collected from a polluted area contained higher concentrations of zinc than larger animals (Ayling 1974). In contrast, Boyden found a direct relationship between zinc accumulation and body weight in *Mercenaria mercenaria*. An increase in zinc concentrations with age, and presumably size, was noted in *M. mercenaria* by Romeril (1974). Hugget et al. (1973) found no correlation between weight and zinc content in *Crassostrea virginica*. Discrepancies may be the result of species differences, sampling error, which may be high, or differences in experimental conditions.

c) Season - Although seasonal differences in body burdens have been observed, no trend is apparent. Bryan (1973) observed the highest concentrations of zinc in two species of scallop in the winter, and attributed this to low primary productivity. Romeril (1974) found increased zinc levels in clams and cockles in May, which then decreased after spawning. Frazier (1975) found zinc levels to be correlated to gonadal development.

d) Other ions - The rate of zinc uptake in Ostrea edulis was depressed by the presence of iron or cobalt, although equilibrium zinc concentrations were similar to controls (Romeril 1971). Apparently, competition was for initial binding sites (Coombs 1972).

Lead

Uptake - The rate of lead uptake is linearly related to water concentration and decreases with time. The body burden attained at equilibrium depends on the concentration of lead in the medium and the exposure time (Schulz -

Baldes 1974, Majori and Petronio 1973). Lead accumulation is not physiologically regulated and appears to be entirely dependent on the amount of metal available (Ayling 1974).

The uptake of lead from food sources has been investigated. Schulz-Baldes (1974) determined that the proportion of available lead accumulated by Mytilus edulis was similar when lead was present in the water or in algae. Abalone fed lead-treated brown algae accumulated the metal and at the end of the experiment contained more lead than the food source (Stewart and Schulz-Baldes 1976).

Localization in tissues - The greatest accumulation of lead in experimental animals occurred in the kidneys and gills (Schulz-Baldes 1974). Digestive glands and mantle tissue contain less.

The highest concentrations of lead in animals collected in the field were found in the kidneys and digestive glands by Bryan (1973) and Schulz-Baldes (1973), although Chow et al. (1976) observed the highest concentrations in the gills. Shells and adductor muscles also contained significant amounts of lead. In some cases the shells contained more than the soft parts because lead can substitute for calcium in the shell matrix.

Other factors affecting uptake

A) Species - Bryan (1973) noted different levels of lead in two species of scallop and Chow et al. (1976) observed body burden differences within the genus Mytilus collected along the California coast. However, Brooks and Rumsby (1965) found a fairly uniform distribution of lead in three species of New Zealand molluscs, including a scallop, a mussel and an oyster. Pringle et al. (1968) also noted uniform levels of lead in oysters and clams.

b) Size and weight - The relationship of size to lead accumulation is controversial. Experiments on lead uptake in several species of molluscs revealed a direct (i.e.power of one) relationship to weight (Boyden 1974). However, Schulz-Baldes (1973) found that small Mytilus edulis contained more lead than large animals and Chow et al. (1976) observed no correlation between lead concentration and body weight.

c) Season - Bryan (1973) found the highest lead concentrations in the winter.

Manganese

Uptake - Most of the work on manganese uptake has been concerned with the radionuclide, ^{54}Mn. The uptake of ^{54}Mn increases with increasing concentration of nuclide, which is rapid at first and then levels off (Harrison 1969, Calapaj and Ongaro 1971). Harrison (1969) found that initial uptake was linearly proportional to concentration up to 1 mg/l; at higher concentrations increases in uptake did not rise proportionately. Uptake of the radionuclide decreased as the concentration of stable manganese in the water increased (Ravera 1964, Calapaj and Ongaro 1971).

Localization in tissues - Ravera (1964) and Merlini (1967) reported that the external tissues of freshwater bivalves, such as gills, mantle and palps, concentrate more manganese than internal tissues such as the digestive gland and stomach, except that the largest concentrations were present in the calcareous tissue. In contrast, Pentreath (1973) and

Bryan (1973) found the highest concentrations of manganese in the internal organs of marine molluscs. It is unknown whether these differences are the result of species or habitat differences or to differences in the tissues examined.

Excretion - The loss of ^{54}Mn from *Anodonta nuttalliana* placed in unlabeled water is bimodal, indicating the existence of differently bound pools of this element. Transfer of the nuclide from the shell to internal organs has been observed (Harrison 1969).

Other factors affecting uptake

a) Species - Several investigators have noted large differences in manganese concentrations in different species (e.g. Brooks and Rumsby 1965, Pringle et al. 1968, Segar et al. 1971).

b) Size and weight - The results of two studies have indicated that the concentration of stable manganese in the freshwater bivalve, *Unio mancus* increases with size (Ravera 1964, Merlini et al. 1965). However, Seagle and Ehlmann (1974) found no correlation between size and manganese concentration in two freshwater species. The inverse relationship between ^{54}Mn concentration and weight in *Anodonta nuttalliana* reported by Harrison (1969) may have occurred because the exchange of the radio nuclide with stable manganese present in the tissues is closely related to surface area phenomena.

c) Season - Galstoff (1942) observed the highest manganese concentration in *Crassostrea virginica* in the summer, which decreased after spawning.

Sex differences in concentration were noted, being higher in ovaries than testes. Frazier (1975) also found elevated levels of manganese in *C. virginica* in the summer. Manganese concentrations were correlated to shell growth, as one might expect.

Bryan (1973) observed the highest concentrations in two species of scallops in the autumn and winter, and related these to low primary production.

Cobalt

Uptake - ^{60}Co concentrations in *Lampsilis radiata* transplanted to the Savannah River paralleled the concentration of this radionuclide in the water (Harvey 1969).

Localization in tissues - Cobalt is most highly concentrated in the kidney, digestive gland and stomach of molluscs; gills and mantle contain moderate amounts and muscle tissue generally has the lowest concentration (Bryan 1973, Pentreath 1973a). However, Segar et al., (1971) found the highest concentrations in the gills and mantle of *Modiolus modiolus* and in the gonad of *Pecten maximus*.

Other factors affecting uptake

a) Species - Segar et al. (1971) found differences in cobalt concentrations which covered an order of magnitude in the eleven species of molluscs they investigated, and Bryan (1973) found differences in two species of scallops. However, Pringle et al. (1968) noted that cobalt concentrations appeared to be similar in several species studied.

b) Season - Bryan (1973) observed the highest cobalt concentrations in molluscs in autumn and winter, and related this to low primary productivity.

Silver

Localization in tissues - Digestive glands contained the highest concentrations of silver in all species studied by Bryan (1973) and Segar et al. (1971).

Species differences - Differences in tissue concentrations of over two orders of magnitude were observed in the whole soft parts of eleven species of marine molluscs investigated by Segar et al. (1971).

Macroinvertebrates (other than molluscs)

Little information concerning heavy metal accumulation in macroinvertebrates is available. Several studies indicated that sediments and food are important sources. The importance of each source is likely to vary from group to group.

Most studies have not investigated the distribution of metals within an organism. Hutchinson et al. (1977) stresses the importance of this, because the adsorption of metals to exoskeletons causes high variability in reported metal levels. Another source of error in measured body burdens is caused by the silt that many benthic organisms carry in their digestive tracts. Values obtained from uncleaned animals may be too high and the error involved can be large (Mathis and Cummings 1973, Elwood et al. 1976).

The results of the experimental studies that have been conducted are presented below.

Copper

Macrocrustaceans - Bryan (1968, 1976) has shown that decapods regulate copper concentrations fairly well. Data in Figure 31 show that crayfish accumulate more copper in polluted areas, but that ranges observed in specimens obtained from these and uncontaminated areas overlap.

Tubificids - Tubificid worms accumulated more copper when fed bacteria that had been previously exposed to copper than when fed unexposed bacteria (Patrick and Loutit 1977).

Insects - Nehring (1976) reported that *Ephemerella grandis* and *Pteronarcys californicum* accumulated copper in proportion to the concentration of copper in the test water. However, it appears that the relationship in the stonefly is linear, whereas accumulation in the mayfly seems to occur at a threshold, which may indicate regulation of copper uptake at low concentrations.

Zinc

Macrocrustaceans - Bryan L1968) presents evidence that decapod crustaceans regulate zinc uptake. The hepatopancreas serves as a storage organ, but excretion takes place via urine or feces. In the freshwater crayfish, *Austropotamobius p. pallipes*, nearly all zinc is excreted in the feces. The data in Figure 34 support the conclusion that zinc is regulated in this group.

Tubificids - Tubificid worms accumulated more ^{65}Zn from water as ambient concentrations and temperature were increased (Dean 1974). Although the author found no accumulation from the sediments, the experimental setup did not permit this conclusion. Tubificids can also accumulate zinc from food sources, such as bacteria (Patrick and Loutit 1976).

Insects - Ephemerella grandis and Pteronarcys californicum accumulated zinc in proportion to water concentrations (Nehring 1976). The relationship is apparently linear in both species. Predictions of zinc concentrations in natural stream conditions using E. grandis proved to be fairly accurate, and the use of transplanted animals to monitor water quality was suggested by the author. This study lasted two weeks, and over longer periods of time, molting may prove to be a problem.

Higher concentrations of zinc than both water and sediments have been found in Chironomids (Mathis and Cummings 1973, Namminga and Wilhm 1977). It is possible that most of the zinc is adsorbed to the surfaces of the animals, and that the low concentration factors reported by Namminga and Wilhm (1977) resulted from losses associated with frequent molts.

Lead

Tubificids - Tubificid worms accumulate lead through the food chain in approximate proportion to the concentration in the food (bacteria) (Patrick and Loutit 1976).

Insects - Ephemerella grandis and Pteronarcys californicum accumulated lead in proportion to concentrations in water (Nehring 1976).

Lead concentrations in crayfish and amphipods from polluted areas appear to be higher than in organisms from unpolluted areas (Figure 35).

Cobalt

Macrocrustaceans - Uptake of ^{60}Co in *Cambarus longulus* was proportional to water concentrations. The exoskeleton accumulated cobalt at a faster rate than the soft parts, indicating that adsorption played an important role. Smaller crayfish contained more cobalt and larger crayfish reached equilibrium sooner (Wiser and Nelson 1964).

Silver

Insects - *Ephemerella grandis* and *Pteronarcys californicum* accumulated silver in proportion to the concentration of silver in test water (Nehring 1976). It appeared that accumulation in the stonefly was linearly related to water concentration, while in the mayfly a threshold response was evident. This indicates that the uptake of silver may be regulated at low ambient concentrations in this species.

Manganese

Tubificids - Tubificids can accumulate manganese through the food chain, incorporating this element in rough proportion to the concentration in the food (Bacteria) (Patrick and Loutit 1976).

Fish

Heavy metal uptake by freshwater fish may take place by absorption at exposed surfaces such as the gills, or by ingestion of dissolved and particulate forms in water and food. Much of the experimental work on the accumulation of metals in fish has been designed to relate the uptake of metals from water to toxic effects caused by the metals. Unfortunately, the study of the contribution of metals in food items to body burdens has been largely neglected. Food intake may well be the most important source of some metals, such as zinc, while others, like cadmium, may pass through the alimentary tract with little absorption occurring.

Attempts to use the concentrations of metals in tissues to predict chronic toxic effects on fish have been hindered by the failure to include food items as a source of metals. Further, some studies were acute tests and no toxic effects were observed at low ambient concentrations. Finally, most cases of pollution involve more than one metal. Eisler and Gardner (1973) have shown that accumulation patterns in the presence of mixtures do not conform to patterns observed for single elements. For these reasons, levels accumulated by fish in these experiments are not reported.

Fish appear to regulate essential elements such as copper and zinc and some fish regulate cadmium uptake at low concentrations.

Copper - Experiments have been performed which compared levels of copper accumulated by gills, kidneys, liver and muscle with data obtained in toxicity bioassay experiments. The results indicate that copper uptake by fish is regulated at concentrations that cause no impairment of growth, survival or reproduction. Accumulation occurs when these concentrations are exceeded.

In the brook trout, *Salvalinus fontinalis*, there was no accumulation of copper in eggs or adults at the "no-effect" concentration in soft water

(9.4 μg Cu/l) over a period of twenty-four months (McKim and Benoit 1974).

Bluegills (Lepomis machrochirus) accumulated up to eight times control levels in the liver at the "no-effect" concentration for adult fish (77 μg Cu/l) (Benoit 1975). However, these differences were not significant, because of the variability. Levels in gills, liver and kidneys were significantly higher at 162 μg Cu/l. Survival of bluegill larvae was reduced at 40 μg/l. At this concentration, significant accumulation occurred only in the gills of adults. These studies were conducted in soft water and lasted twenty-two months.

At concentrations up to 16 μg Cu/l, tissue concentrations in the brown bullhead, Ictalurus nebulosus, remained constant (Brungs et al. 1973) At the sublethal concentrations, 27 and 104 μg Cu/l, an increase was observed. Equilibrium was reached within thirty days, after which no further accumulation occurred for twenty months. The tissues of fish that died at higher test concentrations had similar concentrations to those at the highest sublethal concentration. Further, fish maintained at sublethal concentrations and then transferred to lethal concentrations accumulated more copper than those maintained at the lethal levels throughout. There was no difference between tissue levels of dead and live fish at lethal concentrations.

The stone loach (Noemacheilus barbatulus) regulated copper uptake unless certain ambient concentrations (which were different for different tissues) were exceeded (Solbe and Cooper 1976). Levels in muscle and liver of fish exposed to sublethal (120 μg Cu/l) concentrations were greater but not significantly different than control fish. (Solbe and Cooper 1976). The gills accumulated more copper at this concentration than controls. When ambient copper levels exceeded 290 μg Cu/l, tissue levels increased in the operculum and muscle. With increasing period of survival, tissue concentrations increased and then decreased toward control levels. This phenomenon may explain the low tissue levels attained in fish exposed to the highest concentrations (to 760 μg Cu/l). Tissue levels were similar in fish surviving the test (the controls and 120 μg/l fish) and those that died rapidly in the highest ambient concentrations. Depuration was rapid in all tissues except the liver. The tests lasted sixty days.

The actual levels found in the various tissues differed considerably between species (Benoit 1975, Brungs et al. 1973, McKim and Benoit 1974, Solbe and Cooper 1976). The highest levels were found in livers. Kidneys had the next highest concentration in bluegills and trout, followed by the gills. In bullheads and stone loach, that order was reversed. Brown and Chow (1977) observed similar distributions in fishes from Toronto Harbor.

Although there is some indication that copper accumulation may occur at sublethal levels, it is apparent that copper uptake in fish is fairly well regulated. In addition, the observation by Brungs et al. (1973) that tissue levels may depend on past exposure levels and the fact that these studies ignored other sources of copper available to the fish, make it difficult to adequately interpret the body burdens of specimens collected in natural waters.

Factors Affecting Uptake

a) Species differences - In addition to the differences in tissue levels alluded to above, other authors have noted inter-species variability of copper burdens in field surveys (Bussey et al. 1976). Eisler and La Roche (1972) stressed the need for large sample sizes, owing to great intra-specific variation. However, Northcote et al. (1974) and Lucas et al. (1970) found little or no differences in the copper levels of several species of Fraser River fishes and Great Lakes fishes, respectively.

b) Size - Similar concentrations were found in fish of various lengths by Eisler and LaRoche (1972) and Bussey et al. (1976).

c) Trophic status - Hesse and Evans (1972) found more copper in bottom feeding fish than in predators. The fact that bullheads (Brungs et al. 1973) accumulated less copper than predatory trout (McKim and Benoit 1974) at comparable exposure levels seems contradictory. However, these studies did not account for copper accumulation through the food chain.

Nickel

Accumulation from water - Based on very limited data, it appears that fish do not regulate nickel uptake. Hutchinson et al. (1977) investigated nickel uptake in rainbow trout (Salmo gairdneri) adults and fingerlings. Significent differences in tissue concentrations between control and treated fish occurred at 6400 μg Ni/l, where no adult mortality was observed. Fingerlings accumulated more nickel than adults, and also were subject to higher mortality at the concentrations tested (to 14,700 μg Ni/l).

Nickel levels were highest in the kidneys and liver at the highest treatment concentration. Depuration was rapid when fish were placed in uncontaminated water.

Cadmium

Uptake from water - Several studies have measured the accumulation of cadmium by various species of fish at several ambient concentrations and have related this information to "no-effect" or sublethal levels for those species. Species and references considered are: brook trout (*Salvelinus fontinalis*) (Benoit et al. 1976) largemouth bass (*Micropterus salmoides*) and bluegill (*Lepomis machrochirus*) (Cearley and Coleman 1974); bluegill (*Lepomis machrochirus*) (Eaton 1974, Mount and Stephan 1967); channel catfish (*Ictalurus punctatus*)(Smith et al. 1976); three spine stickleback (*Gasterousteus aculeatus*) (Pascoe and Mattey 1977); zebrafish (*Brachydanio rerio*) (Rehwoldt and Karimian-Teherani 1976); spot (*Leiostomas xanthurus*) (Middaugh et al. 1975) and mummichog (*Fundulus heteroclitus*) Eisler 1971). Tissue levels may be correlated with effects on survival, reproduction, etc. However, strict comparisons of various studies are difficult, even when the same species was used, because of different experimental techniques. Some generalizations can be made. Fish do not regulate cadmium uptake well, if at all. Tissue concentrations increase to equilibrium is achieved at different levels depending on the ambient concentration in the water, being higher at higher concentrations. Concentration factors, where calculated , decrease with increasing concentration.

The greatest accumulation occurs in the kidneys and liver. Gills also accumulate significant quantities. Muscle levels are generally low, which indicates that cadmium may be excluded from non-excretory organs. Detoxification probably occurs in the liver. High concentrations may be observed in the gills during short-term exposures, while levels in the liver may take some time to accumulate. A comparison of the concentrations in these two tissues may give clues as to whether fish have been exposed to recent high levels of pollution or to lower levels for extended periods of time (Mount and Stephan 1967). Cadmium is not readily excreted by fish (Smith and Huckabee 1973, Eisler 1971).

Factors Affecting Uptake

a) Species differences - Species differences in cadmium accumulation were obvious in the papers cited above as well as in several surveys. Bussey et al. (1976) found less cadmium in trout than in other species investigated, a finding which seems to agree with the data of Benoit et al. (1976)and Eaton (1974), although in these studies no equivalent ambient concentrations were used. Cadmium concentrations varied with species and lakes in several Great Lakes fishes (Lucas et al. 1970). Cadmium levels in several species of marine eggs and larvae varied by up to two orders of magnitude (Dethlefsen et al. 1975).

b) Size and weight - Havre et al. (1973) and Bussey et al. (1976) observed no correlation between size or weight and cadmium levels in the tissues of several species. However, Hardisty et al. (1974) found the highest concentrations in larger fish, and suggested that the fish were not excreting the metal.

c) Hardness - Although water hardness may affect the initial uptake rates, it does not appear to affect the final tissue concentrations attained (Mount and Stephan 1967, Kinkade and Erdman 1975).

c) Trophic status - Although no studies were reviewed which attempted to delineate the contributions of different sources of cadmium, the work of Rehwoldt and Karimanian-Teherani (1976) with the zebrafish, *Brachydenio rerio*, is illuminating. Cadmium was administered in the food at levels of up to 10 mg/l. This level, if present in the water, would probably be acutely lethal to the fish, yet they survived and accumulation was less than in other uptake studies. Evidently, much of the cadmium ingested is not assimilated from the digestive system.

Zinc

Uptake from water - Zinc is an essential element and accumulation is regulated in fish tissues. The paper by Mount (1964) deals mainly with a technique for detecting acute zinc-induced mortality. The technique is based on the assumption that the gills accumulate zinc more rapidly at high concentrations than the opercular bone. He suggested the use of a ratio of the concentrations of zinc in the two tissues for the determination of zinc-caused mortality and illustrated its validity for several species. These findings were confirmed by Cairns et al. (1971).

Both studies present data which show accumulation at sublethal concentrations. In the former, most tissues accumulated more zinc with increasing ambient concentrations up to about 3 or 4 mg/l, after which tissue levels declined. The highest concentrations were found in the kidney, bone and skin, while gut and muscle levels remained fairly constant over this range. Cairns et al. (1971) also noted accumulation at sublethal concentrations in acute toxicity tests. In contrast, Eisler (1967) found no differences in whole body concentrations of killifish exposed to sublethal concentrations up to 43 mg/l. At lethal concentrations (157 and 180 mg/l) large increases in tissue concentrations were noted, being lower at the higher concentration. Perhaps this was because they died sooner. Mount (1964) shows that fish do not accumulate zinc after death.

Carp embryos, exposed to various zinc concentrations, attain similar concentrations although they began tests with different initial levels (Sabodash 1970, Vladimirov 1971), suggesting that zinc accumulation is occurring even at these stages.

Factors Affecting Uptake

a) Species differences - Although Bussey et al.(1976) found no significant differences in zinc concentrations in several species, levels were variable. Northecote et al. (1974) found marked species differences in Fraser River fishes and Mount (1964) noted that variation within and between species can be very large.

b) Size - Several authors found higher concentrations of zinc in smaller fish (Eisler and La Roche 1972, Northecote et al. 1974, and Hardisty et al. 1974). Mount (1964) found that size had no effect on gill/bone ratios.

c) Sex - No differences associated with sex were found in the zinc concentrations of marine fishes by Eisler and La Roche (1973).

d) Temperature - Hodson (1975) showed that zinc is taken up more rapidly at higher temperatures, which suggests that uptake is related to metabolism.

e) Trophic status and accumulation via the food chain - The studies cited above addressed the problem of accumulation of zinc from the water. However, it appears that food may be a more important source of this metal to fish. Pentreath (1973, 1976) calculated that the amount of zinc present in water is not sufficient to maintain body zinc levels in adult marine fish and that accumulation from water is insufficient to account for the levels observed in juvenile fish. This is in agreement with Eisler (1967) who observed that marine fish tend to lose zinc to solution at concentrations below 3.5 ppm, and accumulate the metal only at higher concentrations. Apparently, at least in marine fish, the uptake process is somewhat passive.

Hoss (1964) observed that flounder obtained more ^{65}Zn from food than from water, and that when the isotope was present in both forms, the total amount accumulated was equal to the sum of the two sources. A correlation between the zinc concentrations in flounder and the quantity of bivalves (which accumulate zinc to high concentrations) in the diet was observed.

Bottom feeders from contaminated areas contained more zinc than predators, or bottom feeders from uncontaminated environments (Hesse and Evans 1973). High concentrations were found in carp by Mount (1964) and Jen and Huang (1973). Windom and Smith (1973) found similar zinc levels in most of twenty-six species they examined. Highest values were recorded in small planktivorous fish. These results suggest a depletion of zinc in the food chain.

Lead

Uptake from water - The uptake of lead does not appear to be regulated in fish. Accumulation in gills, kidneys and liver of the brook trout, Salvelinus fontinalis, occurred at concentrations below the maximum acceptible toxicant concentration (MATC) determined for this fish (between 58 and 119 μg/l), but not in controls (0.9 μg/l). The rate of accumulation and the maximum tissue concentration attained increased with increasing ambient concentration. Equilibrium was reached in forty-four weeks at the highest concentration (474 μg/l), but uptake continued at lower concentrations (Holcombe et al. 1976).

Adams (1975) investigated the lead body burdens of whole brook trout in a lake subjected to snowmobiling during the winter. Although the concentration of lead in the water reached 135 mg/l, concentrations found in whole fish were considerably lower than those observed in the kidneys, liver and gills of fishes exposed to much lower levels in the aforementioned study. This may be accounted for by the fact that whole fish, which consist largely of muscle, were analyzed. This tissue does not readily accumulate lead (Holcombe et al. 1976). Further, the exposure duration and the actual exposure concentrations are unknown. In laboratory studies with the same species, accumulation was observed at all concentrations greater than controls (4.0 μg/l).

Lead accumulation occurs to the greatest extent in the kidneys, liver, and gills (Holcombe et al. 1976, Bussey et al. 1976, Brown and Chow 1977). Gills may show the highest concentrations in short-term tests (Merlini and

Pozzi 1977a, 1977b). Although few authors have measured the lead content of bone, Pagenkopf and Neuman (1974) observed the highest concentrations in this tissue, where lead can replace calcium as a structural constituent.

Factors Affecting Uptake

a) Age and size - Pagenkopf and Neuman (1974) found increases in the concentrations of lead in gills and bone of trout with size, and the results of Hardisty et al. (1974) showed that larger fish had higher concentrations of lead. These results may indicate that lead is not readily excreted. In contrast, Atchinson et al.(1977)and Pakkala et al. (1972) observed no correlation of lead concentrations to body size.

b) pH - *Lepomis gibbossus* accumulated lead three times more rapidly at low pH 6) than near-neutral (pH 7.5) pH (Merlini and Pozzi 1977a). Merlini and Pozzi (1977b) also report that only lead in the ionic form is accumulated by fish, and stress that little lead remains in this state in natural waters.

Arsenic

Accumulation from water - Accumulation of arsenic in the green sunfish, *Lepomis cyanellus*, increased with increasing exposure concentrations (0 to 60 mg/l), temperature and time (Sorenson 1976). In another experiment, fish were exposed to higher concentrations (100, 500 and 1000 mg/l sodium arsenate (Sorenson 1976). Fish exposed to the lower concentration accumulated less than 50 μg/g dry weight and died between thirty and one hundred twenty-five hours, while those exposed to the two highest concentrations accumulated from 300 to 1400 μg/g dry weight and died within twenty hours. These results indicate that arsenic uptake is not regulated, and that there may be different causes of death at high and low ambient concentrations.

The highest concentrations of arsenic are found in the liver, kidneys and stomach, while lesser amounts are found in the flesh, gills and bones of fish collected in a survey (Bussey et al. 1976). Detoxification probably occurs in the liver. An increase of granules in hepatocytes is observed with increasing exposure level and time (Sorenson 1976c). Intestinal bacteria may convert inorganic arsenic to an organic form. (Penrose 1975).

Factors Affecting Uptake

a) Weight - Sorenson (1976) found no correlation between arsenic uptake and weight.

b) Temperature - As noted above, accumulation increased with increasing temperature (Sorenson 1976).

Silver

Uptake from water - Silver accumulation is probably not regulated in fish. Concentrations of silver in largemouth bass, *Micropterus salmoides* and bluegill, *Lepomis machrochirus*, increased with exposure concentrations from 0.3 to 70 μg Ag/l. Equilibrium was reached within two months at all concentrations tested, but was proportionately less at the higher concentrations. The bass did not survive the highest concentration. (Coleman and Cearley 1974).

BIOLOGICAL PATHWAYS OF HEAVY METALS IN AQUATIC ECOSYSTEMS

The study of heavy metals pathways in aquatic ecosystems deals with the flow of elements through components of the ecosystem. To understand the transfer of elements between biotic compartments, it is necessary to know the sources and availability of the elements to the organisms, the mechanisms of metal uptake, and the fate of the elements within the organisms, that is, how and in what specific organs or parts they are processed. These aspects were discussed in the preceding section.

Two approaches have specifically addressed the problem of the passage of metals through aquatic ecosystems: field surveys and tracer studies in artificial or small pond ecosystems. Field surveys have measured the concentrations of various elements in organisms of different trophic levels. Either these concentrations or calculated concentration factors were compared. In most cases, no food web relationships are demonstrated, and no direct transfer of elements can be inferred. What is actually documented is the compartmentalization of an element within the system. Often, too few organisms at a given trophic level are investigated to make judgments on elemental transfer through food chains. Frequently, comparisons are made between organisms of the same group but occupying different trophic levels. It should be noted that these comparisons refer to general feeding habits, but may not distinguish sources of an element. For example, several studies have demonstrated higher concentrations of various metals in the tissues of bottom-feeding than in predatory fish. Accumulation in the former may be from the diet, but it must be remembered that extensive contact with the sediments may be a more important source in these cases. In general, surveys neglect consideration of uptake, storage and excretion, and regulation of these processes.

Other authors have attempted to determine the fate of elements in artificial or small pond ecosystems by following labelled tracers added to the system. Most of these studies are of relatively short duration, and direct food web relationships are not demonstrated. Extension of the results of these studies to patterns of accumulation of stable metals in natural systems is difficult. What is measured is the initial uptake of the isotope, a portion of which represents exchange with stable elements already present. Excretion studies show that some elements may be bound in non-exchangeable form. Accumulation of isotopes also depends on the stable element concentration of the medium, and there is no assurance that the forms of the two are the same (Pentreath 1973a).

In this section aspects of metal transport within groups of organisms and the relative importance of various heavy metal sources are considered. Surveys which measured metals in several trophic levels and compared body burdens in organisms with different feeding habits are reviewed. Experimental work is also discussed and related to field findings. Heavy metal concentrations found in aquatic organisms were gathered from literature sources for indications of trophic transfer of metals, and these results are compared to surveys and experimental work.

Metal Transport within Groups of Aquatic Organisms

Algae - Accumulation of metals from water by algae most likely includes both passive and active processes. Adaptation to heavy metal pollution has been observed in several species of algae (Stokes, et al. 1973, Say et al. 1977). Increasing tolerance to increasing levels of pollution has been reported (Stocknar and Antia 1976), and may result in greater accumulation of metal contaminants. Rapid algal turnover rates influence the concentrations measured in organisms, especially where ambient metal levels fluctuate significantly. Transport of incorporated metals to the sediments occurs as dead organisms settle to the hypolimnion.

Macrophytes - Aquatic plants can obtain metals from water and sediments, if rooted. However, the extent to which particular metals are translocated from the roots to other plant parts varies (Lee et al. 1976). Attached epifauna and epiflora can contribute significantly to measured concentrations (Patrick and Loutit 1977). At die-off, metals contained in plants can be transported out of stream ecosystems (Valiela et al. 1974, Banus et al. 1975) or deposited in the sediments as detritus. Mathis (1973) found that detritus accumulated greater quantities of metals than live plant parts. This material may serve as an important source of metals for detrital food webs.

Zooplankton - Zooplankton can accumulate metals from water and from ingested food. Much of the measured metal concentrations in these organisms may be associated with the exoskeleton which, when molted, may serve as an important route of transport of heavy metals to the sediments.

Macroinvertebrates - Water, sediments and food may all be sources of metals for organisms in this group. The relative contribution of each has not been well investigated. It is likely that some portion of the heavy metal body burden is associated with the exoskeleton, which may be lost to the sediments or from the ecosystem when molted. Benthic intertebrates may play a significant role in the exchange of elements, including heavy metals, across the sediment-water interface (Wood 1975). Avoidance of polluted sediments has been demonstrated for some groups (Wentsel et al. 1977).

Molluscs - It is generally agreed that food, water and sediments all serve as sources of heavy metals for bivalve molluscs. However, little experimental work has been done to determine the contribution of each (Schulz-Baldes 1974), and there is a lack of agreement as to whether sediments or water are a more important source (Ayling 1974, Merlini et al 1965). While particulate and dissolved metals can be assimilated by bivalves, it is uncertain which contributes most to observed body burdens (Lord et al. 1975). Variable silt burdens may influence the levels measured in bivalves (Preston, et al. 1972). Excretion of metals in feces may be an important means of transport of some metals to the sediments (Andrews and Warren 1969).

Fish - Most of the experimental work on accumulation of metals in fish has considered only water as a source. However, there are indications that, at least for some metals, assimilation from food may be more important (Pentreath 1973b, 1976). Several studies indicate higher levels of several metals in planktivorous and bottom-feeding fishes (Hesse and Evans 1972, Falk et al. 1973) and others indicate a decrease in metal concentrations in fish when compared to crustaceans and insects (Leatherland et al. 1973). Metals associated with the undigestible ecoskeletons may not be readily available, and assimilation in the gastrointestinal tract of fish may be limited. Fish also have a greater capacity to regulate the uptake of many metals than most invertebrates, which may explain the lower concentrations measured.

Pathways of Heavy Metals

Copper - In the few experimental studies that have been conducted, no biomagnification of copper was observed. This conclusion is supported by comparisons of levels in different groups of organisms observed in surveys.

Following application of $CuSO_4$ to a lake, a rapid decrease in the copper content of the water and concurrent incorporation into the sediments occurred. Algae, aquatic plants and fish exhibited rapid uptake of the metal. However, while the macrophytes continued to accumulate copper, levels in fish declined (McIntosh 1975). Copper added to experimental enclosures was rapidly taken up by organisms (algae and zooplankton) (Topping and Windom 1977). Much of the added copper was lost to settlement. This loss was directly related to primary productivity and since copper was found in fecal material, it appeared that little of the copper ingested by zooplankton was assimilated. In an experimental ecosystem, consisting of algae, a mollusc (Tellina) and a fish (plaice), all components showed increased copper levels with increased additions of copper to the water. However, no evidence of biomagnification was observed, and although the fish ate only Tellina siphons, these were low in copper content, and it is likely that most of the copper was accumulated directly from the water (Saward et al. 1975).

Surveys which sampled organisms from different trophic levels point to a general depletion of copper in the food chain (Windom et al. 1973, Jeng and Huang 1973). An apparent concentration of copper from algae to invertebrates has been observed in some cases, but further concentration in higher trophic levels (i.e. fish) does not appear to occur (Kneip and Lauer 1973, Hutchinson et al. 1975). This may result from the ability of fish to regulate copper uptake.

Several points which generally support these conclusions can be drawn from Figures 1, 5, 14, 15, 31 and 38. The highest copper concentrations are found in algae, most being between 350 and 1300 ppm dry weight, which may be the result of the large surface area to volume ratio of algae. Levels in most macrophytes are between 2 and 100 ppm (dry weight). While the bivalve diet is largely composed of phytoplankton, concentrations in bivalves are generally much lower, ranging up to 14 ppm (wet weight) in unpolluted areas and to 80 ppm (dry weight) in polluted locations. Higher values are found in marine molluscs. While macroinvertebrates may obtain some copper from their diet, levels observed are generally low, being between 10 and 40 ppm (dry weight) for insects, gastropods and tubificids. Levels in amphipods and crustaceans may range to 100 ppm. Although some surveys have observed magnification between the algae and invertebrates, it does not seem to be a general trend. High copper levels in fish livers have been observed (to 348 ppm). However, even in polluted areas, levels in fish flesh are considerably lower (to 6 ppm). Fish may be obtaining copper from food organisms, and sequestering it by detoxification in the liver. Accumulation from the food may be occurring, but evidence of biomagnification is lacking.

Nickel - Hutchinson, et al. (1975) found the highest levels of nickel in periphyton, the lowest in fishes. Intermediate levels were found in crayfish, clams, and z ooplankton. Figures 2, 6, 16, 17, 32 and 39 confirm this trend. Algae concentrate nickel to the greatest extent with values ranging between 30 and 130 ppm (dry weight) in unpolluted areas and to 700 ppm in polluted areas. Macrophytes generally have lower levels but may concentrate large amounts in polluted areas. Concentration in freshwater bivalves are quite low (3 ppm wet weight), even in polluted regions. Little data are available for macro-invertebrates. Tubificids may accumulate more than bivalves, possibly because of their close contact with the sediments. Levels in fish from unpolluted areas are similar to those found in invertebrates, and although levels in fish from severely polluted sites may be somewhat higher (10 to 13 ppm) they are still much lower than algal concentrations. Ranges of nickel levels in predatory fish reach higher levels than in bottom-living or planktivorous species.

The contribution of various sources of nickel to organisms is not known, and no evidence of biomagnification has been observed.

Zinc - Experimental studies and surveys lead to the conclusion that although food may be an important source of zinc for many animals, no simple bio - magnification takes place, and depletion through the food chain may occur.

Much of the zinc added to experimental ecosystems or ponds is observed in the sediments (Hannerz et al. 1966,Brungs 1967). Macrophytes and marine algae rapidly accumulate labelled zinc (Hannerz et al. 1966, Duke 1967, Young 1975). Uptake by these organisms can occur from water or sediments, and attached microflora and microfauna may contribute to the zinc levels attained.

Renfro, et al. (1975) found that the fish Gobius sp. accumulated 2.5 times as much ^{65}Zn when the isotope was present in both the water and food organisms than when introduced into the water alone. However, no increase was observed for shrimp or crab. Similarly, it was determined that zinc accumulation from food (Fucus serratus)was more important than accumulation from water in the gastropod Littorina obtusata. However, no biomagnification was observed. Of the invertebrates in an artificial pond to which ^{65}Zn was introduced, chironomids contained the most isotope, possibly because of surface adsorption from the sediments or interstitial water. Interestingly, in this study, predatory pike accumulated more isotope than snails or leeches, although differential feeding may have influenced the ordering of concentrations (Hannerz et al. 1966). Other studies have found the highest concentrations of zinc in bivalves (Duke 1967) and other primary consumers. Predatory fish (bluegill) were observed to accumulate less zinc than carp, snails, leeches and tadpoles (Brungs 1967).

Most survey data lend general support to the above findings. The distribution of zinc concentrations in invertebrates may parallel that of sedentary food items. However, distributions in filter feeders may be anomalous (Ireland 1973). Molluscs may or may not contain more zinc than food items (Leatherland et al. 1973) and bivalves accumulate zinc to higher levels than fish (Jeng and Huang 1973, Leatherland et al. 1973). Among the fishes, food seems to be a more important source of zinc than water (Pentreath 1973b) and higher concentrations are generally found in planktivorous or herbiverous species (Windom et al. 1973), suggesting depletion in the food chain. Northecote et al. (1973) noted exceptions to this statement.

The data plotted in Figures 3, 8, 20, 21, 34 and 41 do not show any obvious trends toward biomagnification. Ranges from group to group show large overlap. Where comparisons are possible, it can be seen that organisms of all groups from polluted waters contain more zinc than those from unpolluted waters, although ranges may overlap.

Cadmium - Results of experiments and surveys point up that there is no simple accumulation up the food chain. Depending on the organisms examined, macrophytes,, insects and/or zooplankton generally have the highest concentrations of cadmium, and fish body burdens are generally lowest. Some exceptions have been observed.

Kinkade and Erdman (1975) introduced ^{115}Cd into an artificial ecosystem and found the highest concentrations in Elodea, which they suggested might be due to the fact that this plant could take up cadmium from both water and sediments. Concentration factors were lower in the alga Nitella and still lower in guppies, snails and catfish in that order. Lu et al.(1975) found that Daphnia, Physa and mosquito larvae all contained more cadmium than fish after the element was sprayed into an experimental pond. In contrast, Smith and Huckabee (1973) observed the highest concentrations in fish in a stream tagged with ^{109}Cd after 42 days. Periphyton concentration factors calculated for periphyton were of similar magnitude although lower than for fish, and in snails they were considerably lower.

Several surveys have observed more cadmium in macrophytes and zooplankton or aquatic insects than in fishes (Ljungren et al. 1971, Mathis and Kevern 1975, Leatherland et al. 1973, Enk and Mathis 1977). In others (c.f. Jeng and Huang 1973), it was noted that bivalves contained more cadmium than fish. Molluscs may or may not accumulate cadmium to higher levels than their diet (Leatherland 1973). The quantities accumulated by aquatic insects do not appear to be related to their feeding habits (Enk and Mathis 1977). Some studies have observed higher concentrations in carnivorous fishes (Enk and Mathis 1977), while others have found higher levels in planktivorous (Windom et al. 1973) or bottom-living (Jaakola et al. 1977) fish. It can be seen in Figure 40 that the highest levels are attained by predatory fish, with the exception of *Carassius auratus*. Inspection of Figures 7, 18, 19, 33 and 40 shows no trend of biomagnification, and, in general, confirms the findings of the above authors. It should be noted that levels in viscera from fish collected in polluted areas can be quite high. However, lower whole body residues would be expected.

Lead - Experimental studies and natural surveys give no indication of biomagnification of lead through food chains. In a pond sprayed with lead, the highest lead concentrations were found in *Daphnia*, *Physa* and mosquito larvae (Lu et al. 1975). Concentrations in fish were considerably lower. Various surveys also indicate that the lowest levels are found in fish. Detritus feeders and grazers, such as snails, and plankton feeders, such as Zooplankton or tadpoles, accumulate lead to the highest concentrations. Predatory aquatic insects occupy an intermediate position (Gale et al. 1973, Jeng and Huang 1973, Mathis and Kavern 1975, Enk and Mathis 1977).

Data presented in Figures 4, 9, 22, 23, 35, and 42 seem to indicate a depletion of lead in the food chain. Primary producers, especially algae, exhibit high levels of lead even in unpolluted sites, and lead burdens in organisms from polluted locations are several orders of magnitude greater than in organisms from uncontaminated locations. Levels in macroinvertebrates are generally lower, although when subject to lead pollution levels may rise by an order of magnitude, possibly due to adsorption to exoskeletons. Levels in fish from polluted areas are low in comparison to other organisms.

Arsenic - Experimental data show that the form of arsenic may influence its uptake by organisms. When introduced as ^{74}As arsenate, uptake in decreasing order was *Gambusia*, *Oedegonium*, *Daphnia* and *Procambarus*, whereas if it was introduced in methylated form as ^{14}C-methanearsonic acid, the order was *Gambusia*, *Daphnia*, *Oedegonium* and *Procambarus*. Apparently, methylation is unnecessary for uptake by fish (Woolson et al. 1976). Perhaps this is because bacteria in the gastrointestinal tract can methylate the arsenic. Also, methylation may interfere with algal uptake. The formation of a non-polar species may reduce adsorption of the initial event in algal uptake of arsenic.

Surveys in natural habitats show a decrease in arsenic levels as one proceeds to higher trophic levels. Kennedy (1976) investigated macroinvertebrates, zooplankton and fish and found no accumulation to higher trophic levels. Ljungren, et al. (1971) observed the highest arsenic concentrations in *Fontinalis* and alderflies; lower values were found in fish, regardless of feeding habits. Leatherland et al. (1973) found lower arsenic levels in fish than in pelagic crustaceans.

The paucity of data in Figures 11, 26 and 44 does not permit any conclusions.

Cobalt - Experiments conducted using labelled cobalt illustrate relative uptake rather than trophic transfer. In a small-scale rice field ecosystem, the order of concentration factors (with respect to the concentration in the water) after the additions of ^{60}Co was rice > omnivorous mud snails > soil > fish (loach, an omnivove) (Honda et al. 1973). The high concentrations observed in rice probably resulted, in part, because the plant can obtain the element from water or soil. Brungs (1967) added ^{60}Co to a freshwater pond and observed a rapid loss to the sediments and to suspended solids. Primary consumers (carp, snails, clams and tadpoles) accumulated higher concentrations than predatory bluegills.

Cobalt concentrations found in several groups of organisms appear to fall in quite similar ranges, between 0.01 and 2 ppm (Figures 10, 24, 25, 36 and 43).

Silver - Transfer of silver through trophic levels. The data presented in Figures 27, 27 abd 45 do not allow any definite conclusions.

Manganese - A survey by Kneip and Mauer (1973) indicated no increase in manganese concentrations in higher trophic levels. The data in Figures 12, 29, 30, 37 and 46 seem to indicate a depletion of the element in the food chain.

Although most organisms accumulate heavy metals, no conclusive evidence of biomagnification through the food chain is available, and no general trends were observed to indicate the occurrence of this phenomenon. As Kneip and Lauer (1973) point out, the acceptance of the concept of biomagnification is based upon rather simplistic assumptions. The concentrations of heavy metals observed in aquatic organisms depends on many factors, not the least of which is the manner in which the organism deals with the element.

The need for experimental studies concerned with the physiology of heavy metal transport is indicated.

THE USE OF AQUATIC ORGANISM TO MONITOR HEAVY METAL POLLUTION

Much of the effort in the study of trace metal body burdens has been directed at the use of aquatic organisms as biomonitors of environmental pollution.. The use of heavy metal body burdens in organisms to monitor environmental quality requires that the quantity of metal accumulated is related to the quantity available in the environment. The availability of heavy metals is determined by the behavior of that metal in water and sediment. This behavior is influenced by several water quality parameters, and the accumulation that takes place at lower trophic levels. The interpretation of heavy metal tissue concentrations depends on an understanding of the kinetics of metal uptake and the processes by which the organism deals with the metal: its use, storage and excretion. These have been discussed in the previous sections. The ability of an organism to regulate the accumulation of heavy metals determines the suitability of that organism as a monitor. If an organism is a good regulator over a given range of environmental concentrations, it cannot serve this function within that range. As previously discussed, fish and decapod crustaceans are good regulators of essential elements, such as copper and zinc, whereas other elements are not as efficiently regulated. Most other organisms, including the bivalve molluscs, the most thoroughly studied group, are poor regulators.

Many investigators have reported levels of various metals in aquatic organisms, and attempted to correlate the body burdens observed and the degree of pollution at particular sites. At best, some general trends can be inferred, and it is the magnitude of differences in the concentrations found in organisms which do not regulate metal accumulation from chronically polluted sites and those found in unpolluted locations that is most revealing.

A major problem in the use of heavy metal body burdens to monitor environmental quality is the great variability that is observed. Most authors have assumed normal frequency distributions of trace metal concentrations in aquatic organisms. However, as Giesy and Wiener (1977) point out, the actual distribution will be determined by uptake and loss kinetics. According to Giesy and Wiener, distributions may be expected to be normal for regulated elements, while skewed and generally log-normal distributions are expected for unregulated ones. Errors in interpretation may result if only means and standard deviations based on assumed normal distributions are reported.

Frequently, the ratio of the concentration of a metal in an organism to the concentration of that metal in the water, the concentration factor, is used to illustrate the degree to which an organism accumulates the metal with respect to ambient levels. However, the concept only applies to steady-state conditions, which probably never occur, and calculation of these factors generally neglects other sources of the metal, such as food items and sediments. For a discussion of concentration factors including several difficulties involved in their application, see Jinks and Eisenbud (1972) and Kneip and Lauer (1973). For these reasons, concentration factors are not discussed in this section.

A more reasonable approach may be the measurement of the uptake rate of organisms transplanted from uncontaminated areas to contaminated ones. The use of this method was advocated and used with some success for algae (Wood 1975), insects (Nehring 1976) and bivalves (Majori and Petronio 1973). The latter of these is the most thorough investigation.

This section presents the results of studies that have attempted to relate the concentrations of heavy metals in organisms to ambient levels. The potential utility of these organisms as monitors of heavy metal pollution is also discussed.

Algae

The accumulation of metals by algae seems to be largely a passive process, although some metabolic control of the uptake of essential elements may occur. Although algae have been found to reflect concentrations of metals in the water in some cases (see below), their use as monitors is restricted by the difficulty of collecting unialgal samples and by the fact that different groups of species are present at different times of the year. A better approach has been suggested by Wood (1975). Unialgal cultures would be maintained in the laboratory and then placed in dacron-polyester bags at selected sites. The resulting data on uptake rates could be used as an indication of the level of pollution in the water. Further, these bags could be used when no local biota are available.

Copper - Wood (1975) found that levels of copper in indigenous algae or in unialgal cultures suspended in natural waters reflected on the level of copper pollution, as measured by water and sediment concentrations, fairly well. Kleeney et al. (1976) found that concentration factors for copper in Cladophora glomerata to be reasonably constant over a range of environmental concentrations. This would indicate that a linear relationship exists between ambient metal levels and accumulation. However, no water concentrations were reported and some data were from other authors. Samples must be taken simultaneously, as fluctuations in water concentrations can result in serious errors in calculated concentration factors. Further, Trollope and Evans (1976) found no linear relation between concentrations of copper in water and concentrations in several species of algae. The data in Figure 1 offer no clarification of this point.

Nickel - Hutchinson et al. (1975) observed that nickel concentrations in algae reflected ambient concentrations in several lakes near Sudbury, Ontario. Trollope and Evans (1976) reported similar findings, however different species were obtained from different sites in this study.

Zinc - Trollope and Evans (1976) observed a linear relationship between cell and ambient zinc concentrations in a Wales mining area, however, because different species were collected from different sites, these results are questionable. Kleeney et al. (1976) reported fairly constant concentration factors for zinc in Cladophora from two areas of Lake Ontario. Since no water levels were presented, it is not known in what range these results are valid. Wood (1975) reported that zinc concentrations in algae adequately reflected ambient (water and sediment) concentrations. At sites where no algae were found, unialgal cultures in plastic bags were utilized.

Cadmium - Kleeney et al. (1976) reported that concentration factors for cadmium in Cladophora glomerata were relatively constant over a range of ambient levels. However, since no water levels were given and it is doubtful that sampling was done simultaneously, these results are questionable.

Lead - The concentration of lead in algae in the "New Lead Belt" in Missouri, was observed to decrease rather abruptly with distance from a metal treatment lagoon (Jennet and Wixson 1975). Much of the lead was trapped by Cladophora. Wood (1975) found that lead concentrations in algae reflected levels of pollution quite well, when compared to sediment concentrations. Lead concentrations in water were not found to be reliable. Other studies (Valiela et al. 1974, Banus et al. 1975) have shown that lead is rapidly incorporated into the sediments. While this could result in reduced availability of the metal to algae, sediment concentrations may better represent the level of pollution to which they are exposed.

Aquatic Macrophytes - Macrophytes can accumulate heavy metals from the water and sediments. Of these two sources, the latter probably provides a better indication of the level of pollution to which local organisms are exposed, because of fluctuations in ambient water concentrations. Positive correlations between metal concentrations in parts of rooted species and in the sediments have been observed in several studies. The part of the plant used in investigations must be considered since the translocation of metals from one part of the plant to another differs for different metals and different species. Plants should be thoroughly washed before analysis, because attached fauna and flora may affect concentration measurements.

Copper - Hutchinson et al. (1975) found large differences in copper concentrations in macrophytes from the area surrounding Sudbury, Ontario. Concentrations in the roots of some species (Eleocharis and Nymphaea) were highly correlated with sediment concentrations, while other species

(*Equisetum* and *Nuphar*) were not. It was suggested that the lack of copper uptake by *Equisetum* may be related to its resistance to metal pollution.

Copper levels in several species appear to be higher in plants collected from sites exposed to copper pollution than from unpolluted sites, although in some cases, ranges overlap (see Figure 5).

Nickel - Hutchinson et al. (1975) found that nickel levels in roots of *Nymphaea* were significantly correlated to sediment levels. This was not true for other plant species. However, when the data were transformed to a log basis, correlations between sediment levels and root concentrations in *Eleocharis* and *Equisetum* were apparent. No correlations between water and macrophyte nickel concentrations were observed.

Kneip et al. (1974) found a significant correlation between concentrations in the roots of *Spartina* and sediment concentrations near a nickel-cadmium battery factory. No significant trends were observed for other plants or plant parts.

As can be seen in Figure 6, most plants exposed to nickel pollution have higher tissue concentrations than those from unpolluted sites, often by two orders of magnitude. However, variability is high and ranges frequently overlap.

Zinc - Gradients of zinc concentrations in plants which parallel those in water and sediments were observed by Hutchinson et al. (1975). However, the data in Figure 8 indicate that, in general, zinc concentrations within a species are similar in plants collected from pollutecd locations. Great interspecific variation of zinc accumulation is evident.

Cadmium - McIntosh et al. (1977) observed the highest cadmium concentrations in Potamogeton crispus in areas with high metal input. A positive correlation between the cadmium concentration in roots of Spartina and sediment concentrations was found by Kneip et al. (1973). However, no significant trends were observed for other species or other parts of Spartina.

No directly comparable data were found in the literature (Figure 7). It appears that plants from polluted locations accumulate cadmium to higher concentrations than plants from unpolluted ones, although ranges may overlap.

Lead - Little comparative data on lead concentrations in aquatic plants are available. However, concentrations in plants from polluted areas are generally two to three orders of magnitude greater than those in plants from uncontaminated locations (Figure 9). A non-rooted plant, Ceratophyllum demersum was transplanted to a lead-polluted lake, and concentrations were observed to increase for six weeks after which they declined (Mayes and McIntosh 1975). This response may have resulted from fluctuations in the lead concentration of the water.

Arsenic - Reay (1972) observed higher concentrations of arsenic in plants from arsenic-rich hot springs than from nearby lakes with low arsenic levels. Only a partial correlation of the concentration of arsenic in the water was found and sediments were not examined.

Invertebrates

Several authors have proposed the use of members of various invertebrate taxa as monitors of heavy metal pollution. For example, Nehring (1976) reported that the uptake of copper, zinc, lead and silver by two insect species was proportional to the respective concentrations of these elements in the test water and found that predictions of metal concentrations on stream water based on the body concentrations of insects transplanted in the stream were good. Hutchinson et al. (1975) found significant positive correlations between the concentrations of copper and nickel in zooplankton samples and water from several lakes in the Sudbury, Ontario region. The use of either of these groups of organisms as monitors is probably limited by the fact that a significant portion of the metal body burdens measured is found in or on the exoskeleton. The process of molting may result in large fluctuations of observed metal concentrations.

More research has been conducted to investigate the feasibility of using bivalve molluscs as monitors of heavy metal pollution because of their sedentary habit, their relatively long life span, and their general inability to regulate the accumulation of metals. However, as will be seen below, results of field investigations are inconsistent. Several cases are presented where metal concentrations in molluscs were correlated to metal levels in water or sediment. However, others report no such relationships and variability may be great. It has been suggested that molluscs may be used only to indicate general trends in pollution (Frazier 1976). Majori and Petronio (1973) have suggested that molluscs with known body burdens be transplanted to polluted areas, and an accumulation factor, a measure of the rate of uptake, be measured. This procedure would concentrate attention on the uptake phase, which may be closely related to ambient levels, and would alleviate the problem of high body burdens caused by the limited excretory mechanisms of the animals. However, sudden, high level discharges could go unnoticed, because of fluctuations in uptake and possible shell closure during periods in which ambient concentrations are high.

Copper - Several studies have shown that bivalves collected near to pollution sources contain higher copper levels than those collected farther away (e.g. Roosenberg 1969, Frazier 1976, Parsons et al. 1973, Alexander and Rowland 1966). Data presented in Figures 14 and 15 tend to support this although, because of high variability, statistically significant differences are not always found and ranges frequently overlap. Further, discrepancies from this trend have been observed. Romeril (1974) found no correlation between copper levels in clams (Mercenaria mercenaria) near a power plant and either sediment or water concentrations. Copper concentrations in mussels (Quadrula quadrula) transplanted to a polluted river decreased steadily downstream from the effluent (Foster 1974). After six weeks the difference between copper concentrations in mussels from downstream stations and those near the effluent source had diminished considerably. Finally, at an abandoned mine site near Cape Rosier, Maine, Mytilus edulis had much greater body burdens than mussels collected at control sites, although copper levels in the water at the two sites were equal (Scott and Major 1964).

Nickel

Navrot et al. (1974) found that nickel levels in Patella vulgata decreased with increasing distance from a power station and Preston et al. (1972) found a general decrease in nickel body burdens in limpets going from inshore to offshore areas.

However, Kneip et al. (1973) found no correlation between nickel concentrations in the mussel, Elliptio complanatus, transplanted to a site near a nickel-cadmium battery operation and water or sediment levels. Alexander and Young (1976) observed no trend in nickel body burdens of Mytilus californianus collected from several sites. Data in Figures 16 and 17 illustrate the range of nickel concentrations found in molluscs.

Zinc - Several studies have indicated that bivalve molluscs from polluted areas have higher concentrations of zinc than organisms of the same species from nearby or adjacent locations. A few examples follow. Ayling (1974) observed the highest concentrations of zinc in Crassostrea gigas taken from the Middle Tamar River where ores had previously been dumped. Body burdens decreased in animals taken from downstream locations. Oysters collected from locations near a zinc-plating plant had higher zinc concentrations than those taken from nearby, unpolluted locations (Ratkowsky et al. 1974). Watson et al. (1961) observed a decrease in the ^{65}-zinc concentrations in several species of marine bivalves as the distance from the mouth of the Columbia River increased. Zinc concentrations in the oyster, Crassostrea commercialis, increased with increasing distance upstream from an estuary, indicating the diluting effect of the estuary (Mackay et al. 1975).

In contrast to these findings, Alexander and Young (1976) found no trend in the zinc body burdens in Mytilus californianus, while the levels of several other metals indicated either diffuse or point sources of pollution. Although zinc levels in Mercenaria mercenaria were highly correlated with sediment concentrations near a power plant outfall, several discrepancies were evident (Romeril 1974).

Both cases are illustrated by the data presented in Figures 20 and 21. Because of the great variability, statistically significant differences would be difficult to obtain. According to Frazier (1976) the use of zinc levels in bivalves can only be used to indicate general trends of zinc pollution.

Cadmium - Body burdens of molluscs taken from polluted areas appear to be higher than those taken from unpolluted areas. Two species of oysters which had similar concentrations at similar locations showed elevated body burdens when taken from areas suffering from increased cadmium levels as a result of pollution from electrolytic zinc plants and ore bodies from wolfram and tin mines (Ratkowsky et al. 1974). Cadmium concentrations in dog whelks (Nucella lapillus) increased after transplantation to regions polluted by smelters. However, even after several months they had not yet reached the concentrations of native whelks (Stenner and Nickless 1974). The concentrations in native whelks were observed to decrease with distance from the smelters. Limpets collected by Preston (1972) from inshore areas had generally higher cadmium body burdens than those taken in offshore areas. However, variability is extremely great, and the ranges of tissue levels in a given species collected from a single area can vary over 2 orders of magnitude (Figures 18 and 19).

Lead - Several authors have noted that lead concentrations in molluscs are higher in animals collected from sites near centers of human activity: cities and coastlines. In these cases, the inputs appeared to be diffuse (Alexander and Young 1976, Chow et al. 1976, Graham 1976, Nielsen and Nathan 1975). Ayling (1974) found higher concentrations of lead in animals near former gold mines, where lead-bearing ores had been dumped. He felt that tissue concentrations could only be used to determine whether conditions were grossly unsuitable for oyster culture. Data presented in Figures 22 and 23 show no consistent pattern of high tissue levels in molluscs from polluted waters, except in *Mytilus edulis*, and *Anodonta* sp. where values are as much as two or three orders of magnitude greater than in mussels from unpolluted waters.

Cobalt - Kneip et al. (1973) observed no correlation between the cobalt concentrations in *Elliptio complanatus* transplanted to a site near a nickel-cadmium battery factory and either sediment or water concentrations. Levels of cobalt observed in several species are given in Figures 24 and 25.

Fish - The use of fish as monitors of heavy metal pollution is limited because of the ability of these organisms to regulate the uptake of several essential metals such as copper and zinc. More critical work is also needed to determine whether they are suitable as monitors of unregulated metals. Knowledge of the dynamics of uptake and elimination is necessary, and the fact that some metals may be sequestered rather than readily excreted confounds the interpretation of metal body burden measurements.

Copper - It appears doubtful that examination of copper levels in fish tissues can provide adequate information concerning environmental pollution. Kelso and Frank (1977) found no differences in levels of copper in sedentary and far-ranging species in Lake Erie. Although copper concentrations were higher in non-migratory fish from Toronto Harbor and a correlation of muscle copper concentrations and sediment levels was obtained (Brown and Chow 1977), tissues from various species were lumped together, and the data are of dubious value. Northecote et al. (1975) observed no differences in muscle copper concentrations related to location in Fraser River fishes, presumably because of their mobility. The data given in Figure 38 show that it is not uncommon for intrapopulation variability to exceed interpopulation variability for a number of species. However, some studies, notably that of Hutchinson et al. (1975), have observed positive correlations of the levels of copper in water and in fish tissue (minnows).

Nickel - While some authors have found higher levels of nickel in fishes exposed to nickel pollution, others have not. Kariya et al. (1968) detected the element in the bodies of fish killed by nickel sulphate and nickel plating solutions and in fish living in these solutions but not in fish living in uncontaminated waters. The levels found in fish from waters suffering from chronic nickel pollution in the Sudbury area (Hutchinson et al. 1977) were orders of magnitude higher than most other values reported. In contrast, Hesse and Evans (1972) observed higher nickel concentrations in bottom feeders from uncontaminated than contaminated locations. They suggested that other pollutants may have interfered with nickel uptake. These latter authors studied previously mined areas, and observed low concentration in fish tissue. These concentrations may have been the result of the relative mobility of nickel in aquatic systems, or low ambient concentrations. Figure 39 shows that except in the Sudbury studies, little difference in tissue levels of fish from contaminated and uncontaminated areas is observed.

Zinc - Fish do not appear to be good indicators of zinc pollution. This is expected of organisms that regulate the uptake of a given substance. Eustace (1974) concurred, observing that fish accumulate little zinc, and are not sensitive indicators of zinc pollution. The data presented in Figure 41 bear this out. While examples may be found where fish from polluted sites contain higher zinc levels than those from uncontaminated areas, the reverse situation has been observed, as have cases where no differences are seen, and concentration ranges frequently overlap.

Two studies in which some correlation of tissue levels to amount of pollution exposure should be mentioned. Atchison et al. (1977) found the levels of zinc in fish from Palestine Lake agreed well with concentrations in the sediments and in water, and higher zinc levels were found in non-migratory fish from polluted Toronto Harbor than in an unpolluted harbor (Brown and Chow 1977).

Cadmium - Smith and Huckabee (1973) cite several examples in which cadmium concentrations in fish tissues exhibited no relationship to sediment or water concentrations. However, the findings of other authors stand in contrast. Jaakala et al. (1972) found higher concentrations in fish from contaminated areas although levels of cadmium in the water were relatively low (10 μg/l). Brown and Chow (1977) found more cadmium in non-migratory fish from polluted Toronto Harbor than from an unpolluted harbor. The data presented in Figure 40 would seem to support the contention that fish collected from polluted areas may contain higher cadmium body burdens. The levels found in several species differ by up to three orders of magnitude when tissues of fish collected from polluted and unpolluted locations are compared.

Lead - Several studies have noted high lead levels in fish from areas subjected to human activities, such as the presence of automobiles and motorboats (Pagenkopf and Neuman 1974, Atchinson et al. 1977, Bussey et al. 1977). However, the data in Figure 42 indicate that lead levels in various species from polluted and unpolluted sites are fairly constant.

Arsenic - Fish do not appear to be suitable monitors of arsenic pollution. Lake Erie fish did not have higher arsenic concentrations than fish from other New York waters, in spite of the fact that arsenic levels in the water were higher (Pakkala et al. 1972). Ullman et al. (1961) found no increase in the levels of arsenic in calico bass from Lake Chautaqua, although an arsenic-containing herbicide had been applied. The authors felt that dispersion and dilution of the toxicant was responsible for this finding.

The data in Figure 44 exhibit no consistent trends. In some cases, fish from polluted areas contain more arsenic than others of the same species from unpolluted locations, but this was not always true. In most cases, tissue concentrations appear to be rather constant.

Other metals - Few studies regarding the use of fish as monitors of pollution by cobalt, silver, manganese or magnesium have been attempted. Figures 43, 45, 46 and 47 show no obvious increases in concentrations in fish from polluted areas, although it is possible that these metals were not important polluting substances.

HEAVY METAL ACCUMULATION BY AQUATIC ORGANISMS IN THE REGIONAL COPPER NICKEL STUDY AREA

Organisms from different trophic levels were collected from several locations throughout the Study Area, including some sites presently affected by heavy metal pollution during 1976 and 1977. Concentrations of several heavy metals in selected tissues from these organisms were measured. The data were collected to determine background levels for organisms at particular sites. Tissue concentrations were compared to those observed in the same species by other authors to ascertain whether levels in organisms of the Study Area were within reported ranges. The relationship between the concentrations of metals found in the organisms to those in the sediments and water was investigated, to assess their suitability as monitors of heavy metal pollution. Finally, a comparison of the metal levels found in different segments of the ecosystem was made to give insight into compartmentalization of metals within aquatic ecosystems.

Sample Collection and Preparation

Fish - In 1976, eighteen species of fish were collected from twelve sites for tissue analysis. Metal levels were determined in these fish to obtain baseline data for comparison with future samples and to appraise the amount of variability between and within species, and between sites, to determine adequate sample size for subsequent collections. Further, based on information from the fishery survey, it was determined which species could most easily be collected in suitable numbers. Based on these considerations, sampling in 1977 was limited to the collection of four species of fish: northern pike, white suckers, yellow perch and walleyes from four study area lakes (Greenwood, Fall, Gabbro and Colby).

Upon collection, fish were wrapped in polyethylene and placed on ice or dry ice, and delivered to the Ecological Services Laboratory (MDNR). Muscle samples were dissected from an area above the lateral line just posterior to the head or, in the case of small fish, whole fillets were used. Liver samples generally consisted of the entire organ, except in large fish, when portions were used. Tissue samples were weighed and freeze-dried. 1977 samples were archived. 0.1 gm. of tissue from 1976 samples were subjected to pressure digestion with nitric acid in a Park^R digestion bomb. Digested samples were analyzed for copper, nickel, zinc, cadmium and lead with a Perkin-Elmer 603 Atomic Absorption Spectrophotometer. For details on the procedures used, see the Tissue Analysis Report (Regional Copper-Nickel Study, 1977).

Invertebrates - Clams, leeches, crayfish and insects were collected from several sites for tissue analysis in 1976. Because samples of the latter three types of organisms generally consisted of a single sample per site and because no species designation was provided, discussion of these results has been omitted from this report. Clams (Anodonta) were collected in sufficient numbers from six sites and are discussed.

Preparation and analysis of clam foot muscle was the same as that described above for fish tissues with the exception that samples were not freeze-dried before digestion. Approximately 0.5 grams (wet weight) tissue was used for analysis.

Macrophytes

Several species of macrophytes were collected and analyzed for heavy metals in 1976. Results were, in general, highly variable. It was decided to use only leaves of *Nuphar variegatum* for analysis in 1977 for several reasons. Data on heavy metal uptake in this species was available in the literature for comparison, and there was some indication that metal uptake by this plant could be related to ambient levels. This species is widespread in the study area, so comparison of different sites would be feasible. Finally, of the plants available throughout the study area, *N. variegatum* is identified to the species level with relative ease.

Leaves of three plants from each of four sites were analyzed for heavy metal concentrations. At two sites, three leaf replicates per plant were used. However, analysis of variance performed on the results indicated that between-leaf variability was significant, while between-plant variability at a given site was not. In subsequent analyses, only one leaf replicate per plant was analyzed.

Leaves were analyzed for copper, nickel, zinc, cadmium, lead, silver, arsenic cobalt, aluminum, manganese, magnesium, iron, titanium, vanadium, beryllium, silicon, zirconium, thorium, calcium, phosphorus, strontium, barium, potassium, chromium, molybdenum, selenium, and sodium by induction coupled plasma emission spectroscopy by Barringer Research, Limited.

Analysis of Data

a. Raw Data:

Metals levels found in fish and clams are available in the Tissue Analysis Report cited above. *Nuphar* levels are available in Copper-Nickel files.

b. Summary charts:

Summary charts for fish, clams and macrophytes are presented in Tables 1 through 3. Only fish species collected from at least four sites were included in the analysis. Included are mean tissue levels for each site, the number of samples that went into calculation of the mean, and mean and median water and sediment concentrations of metals at the collection site or from the nearest available location. For the most part, metal concentrations in water are derived from two years' data gathered by Water Quality Section personnel. In some cases, data from the Leaching/Pathways Section were used, when sites more closely approximated collection sites. Sediment metal levels were obtained from the Leaching/Pathways Section, which collected samples at the 1977 *Nuphar* collections sites. For comparison with fish and clam tissue burdens, values from the nearest available site were used.

Metal levels (copper, nickel, zinc, cadmium and lead) observed in organisms from the Copper-Nickel Study Area were compared with values obtained from the literature (Figures 48-52). Copper-Nickel data are presented as means and ranges for all sites, including currently impacted sites. Literature values for comparison were obtained from figures prepared for the literature review section of this report (1-47) and are given as ranges only. Where possible, the same tissues are used for comparison. Unless otherwise indicated, values are given as ppm wet weight. Means of copper and nickel levels observed in *Nuphar* leaves and *Anodonta* feet from Bob Bay, or currently impacted sites are presented for comparison.

Simple linear regressions were performed to determine the relationship between levels of copper, nickel, zinc, cadmium, and lead in water or sediment and those found in aquatic organisms. The means or levels in tissues were regressed against median water or sediment levels. The correlation coefficients obtained from these regressions are presented in Table 4.

Results and Discussion

Metal levels observed in <u>Nuphar</u> <u>variegatum</u> leaves, Anodonta feet and fish liver and muscle are presented in Tables 1-3. Data

for <u>Nuphar</u>, <u>Anodonta</u> feet and fish liver and muscle are presented in Tables 1-3. Data are given as ppm wet weight for <u>Nuphar</u> and <u>Anodonta</u> and as ppm dry weight for fish tissue. Mean values for each site are presented as well as mean and median values for water and sediments at appropriate sites.

<u>Copper</u> - Data plotted in Figure 48 show that great variability in copper levels was observed in all tissues examined, ranges often exceeded those found in the literature. In general, the upper part of the ranges in tissues from the Study Area were found to be within those observed in polluted or unpolluted areas, and where maximum values exceeded literature values, means were well within previously observed limits. Two exceptions are notable. First, the higher copper levels in <u>Anodonta</u> foot from the Study Area have only been compared to tissues taken from unpolluted locations. Second, while the mean copper level

in black crappie muscle is higher than any previously observed values, the range found in this study overlaps the range of values reported in the literature. Considering the limited amount of information available, the data are in reasonably close agreement with the literature.

Highest copper levels (individual and means) are found in fish liver (especially white sucker and northern pike). On the other hand, levels in fish muscle are generally low, indicating that copper is selectively accumulated by the liver, a finding which agrees with the findings of several authors (e.g. Benoit 1975, Brings et al. 1973, Solbe and Cooper 1976). Nuphar leaves may contain considerable quantities of copper, and the mean is higher than means of fish muscle. Copper content of Anodonta foot is low, possibly because this tissue does not accumulate much copper. The use of other tissues such as the digestive gland or kidneys would probably yield higher values (see Bryan 1973 and Pentreath 1973).

A significant positive correlation between copper content in Nuphar leaves and sediment copper was obtained. The correlation with copper concentration in water was not significant, but was fairly high. Copper in sediments was also significantly correlated with levels in Anodonta foot tissue while the correlation with water was low and slightly negative. This may indicate that the sediments are a more important source of copper than water as Ayling (1974) found or that sedimentary levels more accurately reflect the overall input of copper into the aquatic ecosystem.

No significant correlations were obtained between fish liver and sediment copper content or fish muscle and water copper concentration. White sucker and walleye liver were negatively and positively correlated with water concentrations, respectively. In the latter case, the regression line is nearly horizontal, and it is likely that copper levels are being regulated in this instance. A negative correlation was also observed between white sucker muscle and sediment copper concentrations. Although the slope of this line approaches zero, these data suggest that this fish may be quite efficient in regulating copper uptake or in excreting the metal. Positive correlations were found for northern pike and bluegill muscle and sediments. Of the fish tissues examined, northern pike muscle appears to reflect ambient levels best, increasing consistently with sediment levels. Based on available data, Nuphar leaves would probably be the most suitable biological monitors for copper, and clam tissue may be used, but other clam organs may better serve this task.

The data gathered do not permit conclusions regarding the biological transfer of copper through the food chain. No direct food chain relationships are implied and levels observed depend on the particular tissue examined. Although the highest copper levels were found in fish tissues, macrophytes were also high. Among the fishes studied, levels found in predatory species were quite similar to those in bottom feeders.

Nickel - Nickel levels in all tissues examined varied greatly. The greatest variability, as well as the highest levels attained, were observed in Nuphar leaves. Ranges and means for clam and fish tissue were similar. In most instances, literature data are unavailable. However, where comparisons can be made, the values observed in this study, including those in plants from affected sites, fall within or below the ranges observed by others in polluted areas and agree well with those found in unpolluted areas (Figure 49).

Significant positive correlations were observed for nickel levels in Nuphar leaves and both sediment and water concentrations. Inspection of the data suggests the possibility of using this species as a monitor of environmental nickel levels. Correlations for clam feet were not significant, a result which was expected because it had been shown that muscle tissue in bivalves does not readily accumulate nickel (Bryan 1973).

Nickel concentrations in northern pike and black crappie liver were positively correlated with sediment concentration, and although not significant, the correlation between white sucker liver and sediments was high. Nickel in white sucker and black crappie livers was positively correlated to levels in the water, and similar correlations for walleye and bluegill livers were high but not significant. Nickel concentrations in northern pike muscle were significantly correlated with both sediment and water levels. No other correlations for fish muscle were significant. It is difficult to interpret these results. Information presented in the literature review section of this report indicates that fish probably do not efficiently regulate nickel uptake. The lack of correlations observed in certain cases may be due to insufficient sampling of some species, movement of fishes, etc. For example, these considerations may be important in the case of liver tissue, where some correlations, though not significant, were high. Muscle tissue results generally showed poor correlation. It is possible that at the nickel levels encountered, the element can be selectively restricted from this tissue, with most of the nickel being processed by excretory or storage organs. Northern pike would seem to constitute an exception to this, and further, it is observed that in general the ranges and means of nickel concentrations in liver and muscle appear to be quite similar. Further study is necessary to determine the cause for the observed patterns of accumulation.

Of the organisms investigated, primary producers contained the highest nickel concentrations. From the available data, it does not seem that nickel levels in consumer organisms vary greatly, regardless of their trophic status.

Zinc - Zinc levels found in organisms in the Study Area are generally similar to or lower than levels observed by others in polluted areas and in some cases, unpolluted areas (Figure 50). White sucker livers contained more zinc than reported in other studies, but the data in the literature are limited. The mean zinc content of bluegill liver is lower than that found in unpolluted areas, although the range exceeds literature values.

Of all the regressions performed, the only significant correlation obtained was between white sucker liver and sediment zinc concentration. The regression line is nearly horizontal. Correlations were fairly high but not significant for Nuphar leaves and sediment and water concentrations, and for some fish liver and sediment or water concentrations.

Zinc levels are generally highest in fish livers and means are considerably less in fish muscle. This is consistent with data found in the literature (see Mount 1964). Zinc is accumulated by fish, and its uptake and distribution is probably under physiological control. High levels are also found in Nuphar leaves. Levels in Anodonta were quite low, although bivalves are generally known to accumulate zinc to high concentrations. Bivalve muscle tissue has been found to accumulate zinc to a lesser degree than most other tissues (e.g. Harrison 1969). No definite trends of magnification of higher trophic levels were observed.

Cadmium - Levels of cadmium observed are generally lower than those previously reported in the literature for polluted and unpolluted areas (Figure 51). In a few instances, ranges may extend beyond reported values, but means are well within these. Cadmium levels in black crappie liver are higher than any previously reported for this fish. This may simply be the result of insufficient data to delimit the range of natural variability.

The highest levels of cadmium were found in fish, and the element was more highly concentrated in livers than in muscle. Cadmium is accumulated only slightly in molluscan muscle (Segar et al. 1971) which may account for the lower concentrations found in Anodonta foot tissue. All values for Nuphar leaves were below detection limits. Lee et al. (1976) observed that little translocation of non-essential elements occurred in several species of aquatic macrophytes, which may explain the low cadmium concentration in leaves.

Of all regressions, the only significant correlation found was between the cadmium concentrations in Anodonta foot tissue and water. The general lack of correlations and the overall low levels of cadmium found in all organisms is possibly the result of low levels of cadmium found in the fish tissues, there was also more variability in observed levels. No definite trends were seen regarding accumulation by predatory and non-predatory fish.

Lead - Lead levels in organisms from the Study Area were generally quite low when compared to levels previously reported in the literature(Figure 52). The highest lead levels were found in clam foot tissue. Bivalve muscular tissue can accumulate significant quantities of lead (Bryan 1973, Schultz 1973). All values in *Nuphar* leaves were below detection limits. Lead levels in water are quite low, and the metal is probably not readily transported to the leaves from the roots, which may accumulate more of the element from the sediments or interstitial water. This has been noted for several species of aquatic plants by Lee et al. (1976). Concentrations in fish tissues were low and quite uniform for all species.

Significant positive correlations were found between lead levels in walleye and black crappie liver and water; significant negative correlations were observed between levels in bluegill muscle and sediments and walleye muscle and water. The slope of the regression lines in the latter two cases is very slight. Increased lead concentrations in fish inhabiting lead-polluted waters has been observed by other authors (Bussey et al. 1977, Atchinson et al. 1977).

Conclusions

With few exceptions, mean concentrations of copper, nickel, zinc, cadmium, and lead in tissues of aquatic organisms from the Study Area were similar to values previously reported in the literature (Figures 48-52). In several cases, levels of copper and nickel were somewhat higher, probably reflecting the higher concentrations of these elements at some of the collection sites. On the other hand, observed levels of zinc, cadmium and lead were often somewhat lower than reported values.

Several problems are involved in the interpretation of correlations between metal levels in tissues and the environment. Sample sizes used for computation of mean tissue levels were not equal and often small. The number of sites at which a particular species was collected varied, and sites involved were not always the same. Further, in many cases, the water and/or sediment sites do not correspond exactly to the tissue collection sites, and samples may have been taken at different times. Fish movement may, in some cases, invalidate conclusions. Finally, as mentioned above, the particular tissue examined may influence the results of correlations.

Most of the significant correlations obtained involved copper and nickel (Table 4). The ranges of ambient levels of these metals in water and sediment were much greater than those of the other three metals. At the low environmental levels of these latter metals, uptake patterns may be somewhat obscured, at least in the tissues analyzed.

Nuphar leaves may be suitable as a monitor of copper and nickel levels, as the relationship between tissue levels and ambient levels is proportional and correlations are significant. Further, little destruction to the plant occurs. Accumulation is limited in Anodonta foot tissue, and the fact that stress on clam populations could result if adequate sampling for a monitoring program were performed make this tissue less desirable.

Great variability in fish tissue levels and problems resulting from fish movements would also make adequate sampling difficult.

Concentrations of all metals were always higher in the tissues examined than in water. For the most part, sediment levels exceeded those found in tissues. The most notable exception to this was the high concentration of zinc in nearly all fish liver samples. The essential role of zinc in several enzyme systems and the fairly low levels present in the sediments may account for this relationship. Cadmium concentrations in the liver of several species of fish from some sites were also higher than sediment levels. Cadmium can substitute for zinc, and is probably detoxified in the liver. Finally, in a few cases, copper levels were higher in fish liver than in sediments were observed. These occurred at Birch Lake sites, where copper levels may have been encountered.

However, no conclusions regarding biomagnification can be drawn from the data. As Giesy and Weiner (1977) note, the concentration of an element in whole organisms is the appropriate choice for study of the passage of the element through an ecosystem. Further, a direct food chain relationship must be demonstrated, and sampling for all organisms should be done at the same time. Nevertheless, no trends were seen in the data to indicate that metal levels were greater at higher trophic levels in the Study Area. Indeed, in some cases, the reverse appeared to be true.

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Table 1 Heavy metal concentrations in leaves of *Nuphar variegatum*, water and sediments

METAL	Collection Site	(N)	Water Site	Sediment Site	Mean Tissue Concentration(ppm)	Concentration in Water (ppb)		Concentration in sediments (ppm)	
						mean	median	mean	median
Copper	BB-1	9	LPP/BB-1	LPP/BB-1	4.08	8.15	7.95	82.0	
	BB-2	3	LPP/BB-2	LPP/BB-2	6.96	5.75	5.2	92.0	
	DB-2	9	LPP/DB-2	LPP/DB-2	1.12	2.37	1.8	34.0	
	F-1	3	WQ/F -1	LPP/F-1	10.75	7.75	7.98	273.0	
Nickel	BB-1	9	LPP/BB-1	LPP/BB-1	18.26	67.2	79.0	1100.0	
	BB-2	3	LPP/BB-2	LPP/BB-2	8.23	60.91	69.0	496.0	
	DB-2	9	LPP/DB-2	LPP/DB-2	0.09	2.36	2.0	24.0	
	F-1	3	WQ/F-1	LPP/F-1	1.43	5.60	5.95	76.0	
Zinc	BB-1	9	LPP/BB-1	LPP/BB-1	30.5	2.24	1.50	106.0	
	BB-2	3	LPP/BB-2	LPP/BB-2	21.4	3.426	2.90	60.0	
	DB-2	9	LPP/DB-2	LPP/DB-2	16.7	4.89	3.10	61.0	
	F-1	3	WQ/F-1	LPP/F-1	26.7	4.29	3.43	58.0	
Cadmium	BB-1	9	WQ/BB-1	--	0.07=N.D.	0.037	0.032	--	
	BB-2	3	WQ/BB-1	--	0.07=N.D.	0.037	0.032	--	
	DB-2	9	WQ/D-1	--	0.07=N.D.	0.051	0.031	--	
	F-1	3	WQ/F-1	--	0.07=N.D.	0.047	0.039	--	
Lead	BB-1	9	WQ/BB-1	LPP/BB-1	0.16=N.D.	1.032	0.575	20.0	
	BB-2	3	WQ/BB-1	LPP/BB-2	0.16=N.D.	1.032	0.575	24.0	
	DB-2	9	WQ/D-1	LPP/DB-2	0.16=N.D.	2.187	0.625	20.0	
	F-1	3	WQ/F-1	LPP/F-1	0.16=N.D.	1.097	0.731	16.0	

Table 1 Heavy metal concentrations in leaves of *Nuphar variegatum*, water and sediments. continued

METAL	Collection Site	(N)	Water Site	Sediment Site	Mean Tissue Concentration(ppm)	Concentration in Water (ppb) mean	Concentration in Water (ppb) median	Concentration in sediments (ppm) mean	Concentration in sediments (ppm) median
Cobalt	BB-1	9	LPP/BB-1	LPP/BB-1	0.072	1.50	1.0	47.0	
	BB-2	3	LPP/BB-2	LPP/BB-2	0.016=N.D.	1.24	1.35	23.0	
	DB-2	9	LPP/DB-2	LPP/DB-2	0.016=N.D.	0.57	<0.5	15.0	
	F-1	3	WQ/F-1	LPP/F-1	2.2	0.96	0.99	19.0	
Arsenic	BB-1	9	WQ/BB-1	--	0.14=N.D.	0.63	0.50	—	
	BB-2	3	WQ/BB-1	--	0.14=N.D.	0.63	0.50	--	
	DB-2	9	WQ/D-1	--	0.14=N.D.	0.75	0.80	--	
	F-1	3	WQ/F-1	--	0.14=N.D.	0.82	0.81	—	
Silver	BB-1	9	WQ/BB-1	--	0.002=N.D.	0.046	0.038	—	
	BB-2	3	WQ/BB-1	--	0.065	0.046	0.038	--	
	DB-2	9	WQ/D-1	—	0.002=N.D.	0.029	0.032	--	
	F-1	3	WQ/F-1	—	0.15	0.024	0.022	--	
Aluminum	BB-1	9	WQ/BB-1	--	75.02	63.00	39.50	--	
	BB-2	3	WQ/BB-1	--	50.8	63.00	39.50	--	
	DB-2	9	WQ/DB-2	--	92.8	143.18	99.50	--	
	F-1	3	WQ/F-1	—	41.3	216.88	230.00	—	
Manganese	BB-1	9	LPP/BB-1	LPP/BB-1	178.7	33.2	26.0	1500.0	
	BB-2	3	LPP/BB-2	LPP/BB-2	106.6	57.78	34.0	272.0	
	DB-2	9	LPP/DB-2	LPP/DB-2	650.2	208.0	95.0	1600.0	
	F-1	3	WQ/F-1	LPP/F-1	218.3	68.82	53.33	240.0	

Table 1 Heavy metal concentrations in leaves of *Nuphar variegatum*, water and sediments. continued

METAL	Collection Site	(N)	Water Site	Sediment Site	Mean Tissue Concentration(ppm)	Concentration in Water (ppb) mean	Concentration in Water (ppb) median	Concentration in sediments (ppm) mean	Concentration in sediments (ppm) median
Magnesium	BB-1	9	LPP/BB-1	--	1596.7	31.6	31.2	--	
	BB-2	3	LPP/BB-2	--	1786.7	29.35	35.05	--	
	DB-2	9	LPP/DB-2	--	1492.2	7.82	8.04	--	
	F-1	3	WQ/F-1	--	1856.7	3.35	2.61	--	

Table 2. Heavy metal concentrations in clam (*Anodonta sp.*) foot, water and sediments.

METAL	Collection Site	(N)	Water Site	Sediment Site	Mean Tissue Concentration(ppm)	Concentration in Water (ppb)		Concentration in sediments (ppm)	
						mean	median	mean	median
Copper	Gabbro L-2	3	WQ/LGO-2	LPP/L60-2	0.69	- -	2.0	30.0	29.5
	Birch L-2	6	WQ/LBH-2	LPP/LPH-10	0.78	- -	2.60	22.0	22.0
	LBB-5	6	LPP/BB5	LPP/BB-5	2.08	1.93	1.9	91.67	97.00
	Birch L-4	1	WQ/KC-1	LPP/LBH-4	1.39	2.57	1.95	33.00	33.00
	LDB-2	3	LPP/LDB-2	LPP/LDB-2	0.79	2.87	1.80	24.00	24.00
	LDB-3	6	LPP/LDB-3	LPP/LDB-3	0.80	1.77	1.40	35.00	34.75
Nickel	Gabbro L-2	3	WQ/LGO- 2	LPP/L60-2	0.40	- -	0.80	26.0	26.5
	Birch L-2	6	WQ/LBH-2	LPP/LBH-10	0.33	- -	3.20	46.0	46.0
	LBB-5	6	LPP/BB-5	LPP/BB-5	0.41	8.55	8.00	461.00	502.00
	Birch L-4	1	WQ/KC-1	LPP/LBH-4	0.69	3.46	3.30	39.00	34.00
	LDB-2	3	LPP/LDB-2	LPP/LDB-2	0.51	2.36	2.00	28.50	28.50
	LDB-3	6	LPP/LDB-3	LPP/LDB-3	0.68	2.43	2.0	38.00	35.00
Zinc	Gabbro L-2	3	WQ/LGO-2	LPP/L60-2	10.30	- -	2.0	159.0	154.0
	Birch L-2	6	WQ/LBH-2	LPP/LBH-10	10.10	- -	1.9	202.0	202.0
	LBB-5	6	LPP/BB-5	LPP/BB-5	9.74	2.37	2.73	83.00	83.25
	Birch L-4	1	WQ/KC-1	LPP/LBH-4	9.70	6.84	4.15	70.00	70.00
	LDB-2	3	LPP/LDB-2	LPP/LDB-2	9.50	4.89	3.10	90.00	90.00
	LDB-3	6	LPP/LDB-3	LPP/LDB-3	8.78	1.54	1.60	102.00	102.00
Cadmium	Gabbro L-2	3	WQ/LGO-2	LPP/L60-2	0.06	- -	0.04	--	--
	Birch L-2	6	WQ/LBH-2	LPP/LBH-10	0.07	- -	0.07	1.00	1.00

Table 2. Heavy metal concentrations in Clam (*Anodonta sp.*) foot, water and sediments, continued

METAL	Collection Site	(N)	Water Site	Sediment Site	Mean Tissue Concentration(ppm)	Concentration in Water (ppb)		Concentration in sediments (ppm)	
						mean	median	mean	median
Cadmium	LBB-5	6	WQ/BB-1	LPP/BB-5	0.06	0.037	0.032	0.33	0.25
	Birch L-4	1	WQ/KC-1	LPP/LBH-4	0.07	0.052	0.055	—	—
	LDB-2	3	WQ/D-1	LPP/LDB-2	0.07	0.051	0.031	1.00	1.00
	LDB-3	6	WQ/D-1	LPP/LDB-3	0.05	0.051	0.031	1.33	1.50
Lead	Gabbro L-2	3	WQ/IGO-2	LPP/LGO-2	0.30		0.6	40.0	40.5
	Birch L-2	6	WQ/LBH-2	LPP/LPH-10	0.17		0.3	30.0	30.0
	LBB-5	6	WQ/BB-1	LPP/BB-5	0.20	1.032	0.575	29.0	34.0
	Birch L-4	1	WQ/KC-1	LPP/LPH-4	10.00	0.973	0.825	17.00	17.00
	LDB-2	3	WQ/D-1	LPP/LDB-2	0.73	2.187	0.625	12.00	12.00
	LDB-3	6	WQ/D-1	LPP/LDB-3	0.35	2.187	0.625	25.67	25.25

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments.

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northen Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappe	Walleye
Copper	LBKCB	WQ/KC-1	LPP/LBH-4	2.87(6)	6.5(3)	--	1.3(2)	2.62(3)	3.3(3)
	LBBB	LPP/BB ave	LPP/ave of BB site	18.26(6)	2.7(6)	--	36.3(3)	9.00(1)	19.5(1)
	LBSR	WQ/SR-1	LPP/LBH-10	1.9(4)	6.6(7)	--	5.0(1)	1.48(4)	--
	LBDB	LPP/DB ave	LPP/ave of DB site	3.8(6)	6.5(6)	10.50	--	7.1(6)	--
	KRE	WQ/K-6	--	5.5(6)	3.8(6)	--	7.1(5)	--	--
	K-7	WQ/K-7	--	4.0(6)	3.7(5)	--	--	--	--
	SL-1	WQ/SL-1	--	1.73(2)	--	21.72	--	--	--
	SL-1A	WQ/SL-2	--	3.7(4)	3.43(6)	8.15	--	--	2.5(2)
	P-1	WQ/P-1	--	2.3(6)	2.70(4)	--	--	--	2.38(1)
	Dunka R	WQ/D-2	--	--	4.29(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	6.00	--	--	--
Nickel	LBKCB	WQ/KC-1	LPP/LBH-4	1.21(6)	2.0(3)	--	0.70(2)	1.26(3)	1.8(2)
	LBBB	LPP/BB ave	LPP/ave of BB site	2.1(6)	1.1(6)	--	0.8(6)	0.9(1)	4.3(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.7(4)	0.61(7)	--	1.70(1)	0.95(3)	--
	LBDB	Lpp/DB ave	LPP/ave of DB site	0.48(6)	0.8(6)	2.30	--	1.0(6)	--
	XRE	WQ/K-6	--	0.39(6)	0.25(6)	--	1.4(4)	--	--
	K-7	WQ/K-7	--	0.84(6)	1.1(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.54(2)	--	2.53	--	--	--
	SL-1A	WQ/SL-2	--	1.5(4)	1.55(6)	0.76	--	--	2.4(2)
	P-1	WQ/P-1	--	0.52(6)	0.24(4)	--	--	--	0.6(1)

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northern Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappe	Walleye
Nickel	Dunka R	WQ/D-2	--	--	0.57(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	5.70	--	--	--
Zinc	LBKCB	WQ/KC-1	LPP/LBH-4	17.3(6)	14.3(3)	--	23.9(2)	23.3(3)	24.7(3)
	LBBB	LPP/BB ave	LPP/ave of BB site	28.5(6)	24.4(6)	--	50.(3)	27.0(1)	29.5(1)
	LBSR	WQ/SR-1	LPP/LBH-10	20.9(4)	19.7(7)	--	19.0(1)	19.2(4)	--
	LBDB	LPP/DB ave	LPP/ave of DB site	20.5(5)	20.5(6)	124.50	--	22.7(¢0	--
	KRE	WQ/K-6	--	23.0(6)	40.0(6)	--	31.2(5)	--	--
	K-7	WQ/K-7	--	22.1(6)	21.4(5)	--	--	--	--
	SL-1	WQ/SL-1	--	22.7(2)	--	100.51	--	--	--
	SL-1A	WQ/SL-2	--	29.0([illegible])	20.21(6)	543.48	--	--	19.8(2)
	P-1	WQ/P-1	--	29.2([illegible])	29.6(4)	--	--	--	20.8(1)
	Dunka R	WQ/D-2	--	--	27.1(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	120.75	--	--	--
Cadmium	LBKCB	WQ/KC-1	LPP/LBH-4	0.07(6)	0.07(3)	--	0.12(2)	0.08(3)	0.11(3)
	LBBB	WQ/D-1	LPP/ave of BB site	0.26(6)	0.10(6)	--	0.03(3)	0.05(1)	0.21(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.06(4)	0.10(7)	--	0.07(1)	0.05(4)	--
	LBDB	WQ/D-1	LPP/ave of DB site	0.32(6)	0.16(6)	0.12	--	0.21(6)	--
	KRE	WQ/K-6	--	0.05(6)	0.12(6)	--	0.12(5)	--	--
	K-7	WQ/K-7	--	0.06([illegible])	0.07(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.07	--	0.23	--	--	--
	SL-1A	WQ/SL-2	--	0.11([illegible])	1.89(6)	0.16	--	--	0.18(2)

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n

Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	Concentration in water (ppb) mean	median	Concentration in sediments mean	median
Copper	30.7(6)	43(3)	10.8(2)	19.7(3)	9.5(1)	2.57	1.95	33.00	33.00
	31.9(6)	31.5(1)	410.5(2)	16.0(1)	18.3(1)	3.86	2.80	75.46	76.25
	46.6(4)	100.6(7)	--	14.1(4)	--	0.92	0.89	22.00	22.00
	26.4(6)	61.6(6)	--	12.9(6)	--	2.07	2.05	30.60	33.50
	48.7(6)	73.4(6)	12.7(5)	--	--	1.46	1.49		--
	45.1(6)	66.3(5)	--	--	--	1.65	1.52		--
	35.2(2)	--	--	--	--	2.12	1.67		--
	61.4(4)	77.0(6)	--	--	5.3(2)	1.07	0.90		--
	44.2(6)	25.1(4)	--	--	18.5(1)	3.42	3.38		--
	--	18.0(1)	--	--	--	2.33	1.40		--
	--	--	--	--	--	3.73	3.15		50.00
Nickel	1.1(6)	2.97(3)	1.50(2)	1.20(2)	0.8(1)	3.46	3.3000	39.00	39.00
	2.9(6)	4.9(1)	1.6(1)	2.1(1)	4.6(1)	22.69	11.50	451.39	430.00
	0.47(4)	1.4(7)	--	1.25(4)	--	1.18	0.96	46.00	46.00
	0.59(6)	0.65(6)	--	0.98(6)	--	1.84	2.00	34.20	32.75
	0.66(6)	1.01(6)	1.0(5)	--	--	1.26	0.85		--
	1.3(6)	1.96(5)	--	--	--	1.25	0.96		--
	0.95(2)	--	--	--	--	2.33	1.10		--
	3.6(4)	1.90(6)	--	--	0.9(2)	1.73	1.50		--
	0.76(6)	1.32(4)	--	--	1.2(1)	2.17	1.95		--

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n

						Concentration in water (ppb)		Concentration in sediments	
Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	mean	median	mean	median
Nickel	--	1.09(1)	--	--	--	3.55	3.35	--	
	--	--	--	--	--	103.79	88.50	264.00	
Zinc	206.2(6)	121.5(3)	93.5(2)	104.5(3)	79.5(1)	6.84	4.15	70.00	70.00
	186.8(6)	128.0(1)	316.2(2)	102.5(1)	102.7(1)	2.63	1.70	75.23	80.75
	225.9(4)	175.3(7)	--	89.5(4)	--	3.07	1.68	202.00	202.00
	143.6(6)	137.6(6)	--	93.5(6)	--	2.49	1.70	97.20	99.00
	188.9(6)	146.7(6)	119.2(5)	--	--	1.52	0.03	--	
	127.2(6)	126.4(5)	--	--	--	2.31	1.20	--	
	134.2(2)	--	--	--	--	2.43	2.00	--	
	145.5(4)	133.1(6)	--	--	65.3(2)	3.35	1.85	--	
	172.6(6)	105.3(4)	--	--	86.4(1)	4.66	3.90	--	
	--	114.10(1)	--	--	--	6.18	2.75	--	
	--	--	--	--	--	3.81	2.15	28.00	
Cadmium	0.17(6)	0.86(3)	0.58(2)	1.2(3)	0.36(1)	0.05	0.05	0	0
	0.13(6)	0.45(1)	0.69(2)	1.0(1)	0.24(1)	0.04	0.03	0.39	0.31
	0.25(4)	0.56(7)	--	1.1(4)	--	0.04	0.02	1.00	1.00
	0.12(6)	0.91(6)	--	0.91(6)	--	0.05	0.03	1.20	1.33
	0.24(6)	1.1(6)	4.7(5)	--	--	0.04	0.03	--	
	0.31(6)	0.76(5)	--	--	--	0.04	0.02	--	
	0.25(2)	--	--	--	--	0.05	0.04	--	
	0.29(4)	1.75(6)	--	--	0.11(2)	0.05	0.02	--	

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n

Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	Concentration in water (ppb) mean	median	Concentration in sediments mean	median
Cadmium	0.28(6)	0.35(4)	--	--	--	0.12	0.05	--	
	--	0.27(1)	--	--	--	0.12	0.05	--	
	--	--	--	--	--	0.04	0.03	0	
Lead	0.68(6)	0.75(3)	0.65(3)	1.37(3)	0.80(1)	0.97	0.83	17.00	17.00
	1.4(6)	0.90(1)	0.8(1)	1.0(1)	0.27(1)	1.03	0.58	20.39	18.00
	1.05(4)	1.17(7)	--	0.85(4)	--	0.64	0.49	30.00	30.00
	0.65(6)	0.77(6)	--	0.84(4)	--	2.19	0.63	20.20	22.75
	0.51(6)	0.88(6)	0.57(5)	--	--	0.51	0.31	--	
	0.87(6)	1.20(5)	--	--	--	0.57	0.40	--	
	0.49(2)	--	--	--	--	1.07	0.70	--	
	0.82(4)	0.59(6)	--	--	0.03	0.74	0.41	--	
	0.64(6)	0.70(4)	--	--	0.68(1)	1.12	0.80	--	
	--	0.70(1)	--	--	--	0.95	0.75	--	
	--	--	--	--	--	1.03	0.58	0	

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments.

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northen Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappe	Walleye
Cadmium	P-1	WQ/P-1	--	0.09(6)	0.11(4)	--	--	--	0.18(2)
	Dunka R	WQ/D-2	--	--	0.07(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	0.10	--	--	--
Lead	LBKCB	WQ/KC-1	LPP/LBH-4	0.65(6)	0.66(3)	--	0.50(2)	0.70(3)	0.50(3)
	LBBB	WQ/D-1	LPP/ave of BB site	0.48(6)	0.43(6)	--	0.5(3)	0.50(1)	0.90(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.50(4)	0.80(7)	--	0.4(1)	0.70(4)	--
	LBDB	WQ/D-1	LPP/ave of DB site	0.41(6)	0.74(6)	0.60	--	0.61(6)	--
	KRE	WQ/K-6	--	0.33(6)	0.43(6)	--	0.8(5)	--	--
	K-7	WQ/K-7	--	0.80(6)	0.63(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.40(2)	--	0.91	--	--	--
	SL-1A	WQ/SL-2	--	0.60(4)	0.59(6)	0.43	--	--	0.65(2)
	P-1	WQ/P-1	--	0.74(6)	0.58(4)	--	--	--	0.48(1)
	Dunka R	WQ/D-2	--	--	0.38(1)	--	--	--	--
	EM-1	WQ/BB1	LPP/EM-1	--	--	0.30	--	--	--

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n

Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	Concentration in water (ppb) mean	median	Concentration in sediments mean	median
Cadmium	0.28(6)	0.35(4)	--	--	--	0.12	0.05	--	
	--	0.27(1)	--	--	--	0.12	0.05	--	
	--	--	--	--	--	0.04	0.03	0	
Lead	0.68(6)	0.75(3)	0.65(3)	1.37(3)	0.80(1)	0.97	0.83	17.00	17.00
	1.4(6)	0.90(1)	0.8(1)	1.0(1)	0.27(1)	1.03	0.58	20.39	18.00
	1.05(4)	1.17(7)	--	0.85(4)	--	0.64	0.49	30.00	30.00
	0.65(6)	0.77(6)	--	0.84(4)	--	2.19	0.63	20.20	22.75
	0.51(6)	0.88(6)	0.57(5)	--	--	0.51	0.31	--	
	0.87(6)	1.20(5)	--	--	--	0.57	0.40	--	
	0.49(2)	--	--	--	--	1.07	0.70	--	
	0.82(4)	0.59(6)	--	--	0.03	0.74	0.41	--	
	0.64(6)	0.70(4)	--	--	0.68(1)	1.12	0.80	--	
	--	0.70(1)	--	--	--	0.95	0.75	--	
	--	--	--	--	--	1.03	0.58	0	

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments.

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northern Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappie	Walleye
Cadmium	P-1	WQ/P-1	--	0.09(6)	0.11(4)	--	--	--	0.18(2)
	Dunka R	WQ/D-2	--	--	0.07(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	0.10	--	--	--
Lead	LBKCB	WQ/KC-1	LPP/LBH-4	0.65(6)	0.66(3)	--	0.50(2)	0.70(3)	0.50(3)
	LBBB	WQ/D-1	LPP/ave of BB site	0.48(6)	0.43(6)	--	0.5(3)	0.50(1)	0.90(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.50(4)	0.80(7)	--	0.4(1)	0.70(4)	--
	LBDB	WQ/D-1	LPP/ave of DB site	0.41(6)	0.74(6)	0.60	--	0.61(6)	--
	KRE	WQ/K-6	--	0.33(6)	0.43(6)	--	0.8(5)	--	--
	K-7	WQ/K-7	--	0.80(6)	0.63(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.40(2)	--	0.91	--	--	--
	SL-1A	WQ/SL-2	--	0.60(4)	0.59(6)	0.43	--	--	0.65(2)
	P-1	WQ/P-1	--	0.74(6)	0.58(4)	--	--	--	0.48(1)
	Dunka R	WQ/D-2	--	--	0.38(1)	--	--	--	--
	EM-1	WQ/BB1	LPP/EM-1	--	--	0.30	--	--	--

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n.

Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	Concentration in water (ppb) mean	median	Concentration in sediments mean	median
Nickel	--	1.09(1)	--	--	--	3.55	3.35	--	
	--	--	--	--	--	103.79	88.50	264.00	
Zinc	206.2(6)	121.5(3)	93.5(2)	104.5(3)	79.5(1)	6.84	4.15	70.00	70.00
	186.8(6)	128.0(1)	316.2(2)	102.5(1)	102.7(1)	2.63	1.70	75.23	80.75
	225.9(4)	175.3(7)	--	89.5(4)	--	3.07	1.68	202.00	202.00
	143.6(6)	137.6(6)	--	93.5(6)	--	2.49	1.70	97.20	99.00
	188.9(6)	146.7(6)	119.2(5)	--	--	1.52	0.03	--	
	127.2(6)	126.4(5)	--	--	--	2.31	1.20	--	
	134.2(2)	--	--	--	--	2.43	2.00	--	
	145.5(4)	133.1(6)	--	--	65.3(2)	3.35	1.85	--	
	172.6(6)	105.3(4)	--	--	86.4(1)	4.66	3.90	--	
	--	114.10(1)	--	--	--	6.18	2.75	--	
	--	--	--	--	--	3.81	2.15	28.00	
Cadmium	0.17(6)	0.86(3)	0.58(2)	1.2(3)	0.36(1)	0.05	0.05	0	0
	0.13(6)	0.45(1)	0.69(2)	1.0(1)	0.24(1)	0.04	0.03	0.39	0.31
	0.25(4)	0.56(7)	--	1.1(4)	--	0.04	0.02	1.00	1.00
	0.12(6)	0.91(6)	--	0.91(6)	--	0.05	0.03	1.20	1.33
	0.24(6)	1.1(6)	4.7(5)	--	--	0.04	0.03	--	
	0.31(6)	0.76(5)	--	--	--	0.04	0.02	--	
	0.25(2)	--	--	--	--	0.05	0.04	--	
	0.29(4)	1.75(6)	--	--	0.11(2)	0.05	0.02	--	

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northern Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappe	Walleye
Nickel	Dunka R	WQ/D-2	--	--	0.57(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	5.70	--	--	--
Zinc	LBKCB	WQ/KC-1	LPP/LBH-4	17.3(6)	14.3(3)	--	23.9(2)	23.3(3)	24.7(3)
	LBBB	LPP/BB ave	LPP/ave of BB site	28.5(6)	24.4(6)	--	50.(3)	27.0(1)	29.5(1)
	LBSR	WQ/SR-1	LPP/LBH-10	20.9(4)	19.7(7)	--	19.0(1)	19.2(4)	--
	LBDB	LPP/DB ave	LPP/ave of DB site	20.5(6)	20.5(6)	124.50	--	22.7(c0	--
	KRE	WQ/K-6	--	23.0(6)	40.0(6)	--	30.2(5)	--	--
	K-7	WQ/K-7	--	22.1(6)	21.4(5)	--	--	--	--
	SL-1	WQ/SL-1	--	22.7(2)	--	100.51	--	--	--
	SL-1A	WQ/SL-2	--	29.0(4)	20.21(6)	543.48	--	--	19.8(2)
	P-1	WQ/P-1	--	29.2(6)	29.6(4)	--	--	--	20.8(1)
	Dunka R	WQ/D-2	--	--	27.1(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	120.75	--	--	--
Cadmium	LBKCB	WQ/KC-1	LPP/LBH-4	0.07(6)	0.07(3)	--	0.12(2)	0.08(3)	0.11(3)
	LBBB	WQ/D-1	LPP/ave of BB site	0.26(6)	0.10(6)	--	0.03(3)	0.05(1)	0.21(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.06(4)	0.10(7)	--	0.07(1)	0.05(4)	--
	LBDB	WQ/D-1	LPP/ave of DB site	0.32(6)	0.16(6)	0.12	--	0.21(6)	--
	KRE	WQ/K-6	--	0.05(6)	0.12(6)	--	0.12(5)	--	--
	K-7	WQ/K-7	--	0.06(6)	0.07(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.07	--	0.23	--	--	--
	SL-1A	WQ/SL-2	--	0.12(4)	1.89(6)	0.16	--	--	0.18(2)

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments. continued

Mean concentration in liver (ppm dry weight) ()=n

Metal	Northern Pike	White Sucker	Blue-gill	Black Crappie	Walleye	Concentration in water (ppb) mean	Concentration in water (ppb) median	Concentration in sediments mean	Concentration in sediments median
Copper	30.7(6)	43(3)	10.8(2)	19.7(3)	9.5(1)	2.57	1.95	33.00	33.00
	31.9(6)	31.5(1)	410.5(2)	16.0(1)	18.3(1)	3.86	2.80	75.46	76.25
	46.6(4)	100.6(7)	--	14.1(4)	--	0.92	0.89	22.00	22.00
	26.4(6)	61.6(6)	--	12.9(6)	--	2.07	2.05	30.60	33.50
	48.7(6)	73.4(6)	12.7(5)	--	--	1.46	1.49	--	
	45.1(6)	66.3(5)	--	--	--	1.65	1.52	--	
	35.2(2)	--	--	--	--	2.12	1.67	--	
	61.4(4)	77.0(6)	--	--	5.3(2)	1.07	0.90	--	
	44.2(6)	25.1(4)	--	--	18.5(1)	3.42	3.38	--	
	--	18.0(1)	--	--	--	2.33	1.40	--	
	--	--	--	--	--	3.73	3.15	50.00	
Nickel	1.1(6)	2.97(3)	1.50(2)	1.20(2)	0.8(1)	3.46	3.3000	39.00	39.00
	2.9(6)	4.9(1)	1.6(1)	2.1(1)	4.6(1)	22.69	11.50	451.39	430.00
	0.47(4)	1.4(7)	--	1.25(4)	--	1.18	0.96	46.00	46.00
	0.59(6)	0.65(6)	--	0.98(6)	--	1.84	2.00	34.20	32.75
	0.66(6)	1.01(6)	1.0(5)	--	--	1.26	0.85	--	
	1.3(6)	1.96(5)	--	--	--	1.25	0.96	--	
	0.95(2)	--	--	--	--	2.33	1.10	--	
	3.6(4)	1.90(6)	--	--	0.9(2)	1.73	1.50	--	
	0.76(6)	1.32(4)	--	--	1.2(1)	2.17	1.95	--	

Table 3. Heavy metal concentrations in fish muscle and liver, and water and sediments.

Mean concentration in muscle (or composite) (ppm dry weight) ()=N

Metal	Collection Site	Water Site	Sediment Site	Northern Pike	White Sucker	White Sucker Composite	Blue-Gill	Black Crappe	Walleye
Copper	LBKCB	WQ/KC-1	LPP/LBH-4	2.87(6)	6.5(3)	--	1.3(2)	2.62(3)	3.3(3)
	LBBB	LPP/BB ave	LPP/ave of BB site	18.26(6)	2.7(6)	--	36.3(3)	9.00(1)	19.5(1)
	LBSR	WQ/SR-1	LPP/LBH-10	1.9(4)	6.6(7)	--	5.0(1)	1.48(4)	--
	LBDB	LPP/DB ave	LPP/ave of DB site	3.8(6)	6.5(6)	10.50	--	7.1(6)	--
	KRE	WQ/K-6	--	5.5(6)	3.8(6)	--	7.1(5)	--	--
	K-7	WQ/K-7	--	4.0(6)	3.7(5)	--	--	--	--
	SL-1	WQ/SL-1	--	1.73(2)	--	21.72	--	--	--
	SL-1A	WQ/SL-2	--	3.7(4)	3.43(6)	8.15	--	--	2.5(2)
	P-1	WQ/P-1	--	2.3(6)	2.70(4)	--	--	--	2.38(1)
	Dunka R	WQ/D-2	--	--	4.29(1)	--	--	--	--
	EM-1	WQ/BB-1	LPP/EM-1	--	--	6.00	--	--	--
Nickel	LBKCB	WQ/KC-1	LPP/LBH-4	1.21(6)	2.0(3)	--	0.70(2)	1.26(3)	1.8(2)
	LBBB	LPP/BB ave	LPP/ave of BB site	2.1(6)	1.1(6)	--	0.8(6)	0.9(1)	4.3(1)
	LBSR	WQ/SR-1	LPP/LBH-10	0.7(4)	0.61(7)	--	1.70(1)	0.95(3)	--
	LBDB	Lpp/DB ave	LPP/ave of DB site	0.48(6)	0.8(6)	2.30	--	1.0(6)	--
	XRE	WQ/K-6	--	0.39(6)	0.25(6)	--	1.4(4)	--	--
	K-7	WQ/K-7	--	0.84(6)	1.1(5)	--	--	--	--
	SL-1	WQ/SL-1	--	0.54(2)	--	2.53	--	--	--
	SL-1A	WQ/SL-2	--	1.5(4)	1.55(6)	0.76	--	--	2.4(2)
	P-1	WQ/P-1	--	0.52(6)	0.24(4)	--	--	--	0.6(1)

Table 4. Correlation coefficients derived from regressions of tissue, sediment and water on metal concentrations.
() = number of points in regression.

Tissue / Metal	Nuphar leaves	Anodonta foot	FISH LIVER					FISH MUSCLE				
			White sucker	Northern pike	Walleye	Blue-gill	Black crappe	White sucker	Northern pike	Walleye	Blue-gill	Black crappe
$Cu_{tissue}Cu_{H_2O}$	.6951(4)	.2082	-.6906*(9)	-.4917(9)	.9435*	.9368(3)	.2381(4)	-.2914(9)	.3833(9)	.2596(4)	.7873(4)	.8703(4)
$Cu_{tissue}Cu_{sed}$	.9218*(4)	.9072**	-.7586(4)	-.3638(4)	---	---	.1404(4)	-.9803**(4)	.9900**(4)	---	.9585*(3)	.8201(4)
$Ni_{tissue}Ni_{H_2O}$	.9146*(4)	-.2111	.8604*(9)	.5071	.8697(4)	.7841(3)	.9465*(4)	.2107(9)	.8048**(9)	.3749(4)	-.6595(4)	-.3587(4)
$Ni_{tissue}Ni_{sed}$	.9997**(4)	.2300	.8615(4)	.9682**(4)	---	---	.9769**(4)	-.0343(4)	.9080*(4)	---	-.4051(3)	-.5344(4)
$Zn_{tissue}Zn_{H_2O}$	.6115(4)	-.0422	-.6028(9)	.2487(9)	.6158(4)	-.3265(3)	.6556(4)	-.3499(9)	-.0366(9)	.3189(4)	-.2637(4)	.0586(4)
$Zn_{tissue}Zn_{sed}$	.6997(4)	.5498	.9968**(4)	.5086(4)	---	---	-.8589(4)	.0919(4)	-.0979(4)	---	-.5628(3)	-.8199(4)
$Cd_{tissue}Cd_{H_2O}$	---	.8595*	-.4115(9)	-.2912(9)	.5229(4)	-.5701(3)	.2719(4)	-.3773(9)	-.1073(9)	-.7677(4)	.4859(4)	-.0369(4)
$Cd_{tissue}Cd_{sed}$	---	-.2955	.1817(4)	.0710(4)	---	---	.1709(4)	.8661(4)	.4021(4)	---	-.3632(3)	.6240(4)
$Pb_{tissue}Pb_{H_2O}$	---	.6957	-.4490(9)	-.1666(9)	.9879**(4)	.3634(3)	.8873*(4)	.0185(9)	.2187(9)	-.9815**(4)	-.5914(4)	.2616(4)
$Pb_{tissue}Pb_{sed}$	---	-.4731	.8168(4)	.0196(4)	---	---	-.7183	.7276(4)	-.4089(4)	---	-.9976**(3)	.4226(4)

* significant at α .05
** significant at α .01

Note on the Preparation of Figures 1-47

Literature sources were culled to provide a summary of heavy metal levels observed in tissues of aquatic organisms. These summarized data were then placed in Figures 1-47. These figures are intended as a reference of background levels for comparison. Only data in readily-accessible form were used. Unfortunately, several reports with considerable information were omitted because the data had not been summarized.

Data are presented by species; values for lumped groups such as "algae" were omitted. Different tissues are plotted with separate lines. The concentration term (wet or dry weight) is the same for all lines on a graph unless otherwise noted on the graph by a "w" or "d". For comparisons, Ayling (1974) notes that wet weight values are approximately equal to 0.2 dry weight values. Data gathered by the Regional Copper-Nickel Study confirm this approximation for fish. Levels in terms of wet weight were from 0.2 to 0.3 times those in terms of dry weight. Except for groups or metals where available data were limited, data which did not indicate species, tissue or whether wet or dry weight was used were omitted.

The data are plotted as ranges, with all available information included in the range. If only a mean and standard deviation was available, the mean is indicated and the standard deviation is given as a range.

It is common that the upper extremes of ranges represent only a few samples while the majority of values are considerably less. This may be especially true for metals whose uptake is unregulated. Giesy and Weiner (1977) point out that distributions of these metals are likely to be non-normal and positively skewed. The extremes may, in some cases, be more important quantities to measure than means.

Ranges for organisms from unpolluted, generally polluted and polluted areas are given. Unpolluted areas are those in which no known pollution had occurred. Areas receiving general pollution are those receiving unspecified wastes, such as rivers below municipalities which may receive a large variety of contaminants. Areas designated as polluted are those that were at the time of sampling, or had been exposed to metal wastes. However, even in these areas, the designation does not necessarily imply that the particular metal under consideration was available as a pollutant. Frequently, metals measured in organisms were not measured in water or sediments, so it was impossible to determine if specific pollution by that metal existed. These difficulties may have resulted in some apparent discrepancies in the charts, such as tissue concentrations higher in organisms from unpolluted areas than from polluted areas. On the other hand, as noted in the body of this report, many of these discrepancies are probably real.

Great variability will be noted in the charts. In part, this variability is inherent in biological sampling. Other contributing sources are the following: 1) Differences in methods of metal analysis and laboratory techniques can result in substantial differences in measured concentrations. 2) Differences in substrates and water quality parameters may affect the availability of metals for uptake. 3) Degrees of pollution encountered vary considerably, and results may be expected to vary accordingly.

References are identified by numbers adjacent to each which refer to the following list of citations.

Citations for Figures 1-47

Algae (Figs. 1-4)

2) Trollope and Evans 1976
3) Kleeney et al. 1976
4) Gale et al. 1973

Macrophytes (Figs. 5-13)

1) Reay 1972.
2) Stenner and Nickless 1974.
3) Mathis and Kevern 1975.
4) Gale et al. 1973.
5) Jennet and Wixson 1975.
6) Ljunggren et al. 1971.
7) Varenko and Chuiko 1971.
8) Hutchinson et al. 1975.
9) Fitchko 1977,(unpublished data).
10) Linn et al. 1973.
11) Riemer and Toth 1969.
13) McIntosh 1975.
14) Adams et al. 1973.

Macroinvertebrates (Other than bivalves) (Figures 31-37)

1) Ljunggren et al. 1971.
2) Mathis and Kevern 1975.
3) Brown 1976.

4) Anderson 1977.

5) Mathis and Cummings 1973.

6) Gale et al. 1973.

7) Merlini et al. 1965.

8) Enk and Mathis 1977.

Molluscs - freshwater (Figures 14, 16, 18, 20, 22, 24, 25, 26, 27 and 29)

1) Segar et al. 1971.

2) Mathis and Cummings 1973.

3) Lord et al. 1975.

4) Foster 1974.

5) Pauley and Nakatani 1968.

Molluscs - marine (Figures 15, 17, 19, 21, 23, 28 and 30).

1) Alexander and Rowland 1966.

2) Sims and Presley 1976.

3) Frazier 1976.

4) Pringle et al. 1968.

5) Wolfe 1970.

6) Ferrel et al. 1973

7) Ratkowsky et al. 1974.

8) Ayling 1974.

9) Thrower and Eustace 1973.

10) Jeng and Huang 1973.

11) Watling and Watling 1976.

12) Coombs 1972.

13) Nielson and Nathan 1975.

14) Brooks and Rumsby 1965.

15) Bryan 1973.

16) Segar et al. 1971.

17) Stenner and Nickless 1974.

18) Pentreath 1973a.

19) Mackay et al. 1975.

20) Zook et al. 1976

21) Sidwell and Loomis 1976 (cited in Zook et al. 1976)

22) Windom and Smith, 1972.

23) Talbot et al. 1976.

24) Chow et al. 1976.

Fish (Figures 38-47).

1) Copeland et al. 1973

2) Bussey et al. 1976.

3) Tong et al. 1972.

4) Michigan WRC 1972.

5) Hutchinson et al. 1975.

6) Mathis and Cummings 1973.

7) Uthe and Bligh 1971.

8) Jeng and Huang 1973.

9) Lucas et al. 1970.

10) Hartung 1972.

11) German 1972.

12) Van Meter 1974.

13) Armstrong and Lutz 1974.

14) Kelso and Frank 1974.

15) McIntosh 1975.

16) Kleinert et al. 1974.

17) Pakkala et al. 1972a, b.

18) Traversy et al. 1975.

19) Zook et al. 1976.

20) Enk and Mathis 1977.

21) Mathis and Kevern 1975.

22) Atchison 1975.

22b) Atchison et al. 1977.

23) Mount 1964.

24) Lovett et al. 1972.

25) Jaakkala et al. 19

26) Havre et al. 1973.

27) Ljunggren et al. 1971.

28) Smith et al. 1976.

Figures 48-52. Heavy metals in Aquatic Organisms of the Regional Copper-Nickel Study Area.

Means and ranges of concentrations of copper- nickel, zinc, cadmium and lead in aquatic organisms from the Regional Copper-Nickel Study Area and ranges of concentrations observed in the same organisms collected from polluted and unpolluted locations as reported in the literature. Values are taken from Regional Copper-Nickel Study data and Figures 1-47.

Legend:

————————	Range of concentrations found in organisms from unpolluted locations, as reported in the literature.
— — — — — —	Range of concentrations found in organisms from polluted locations, as reported in the literature.
▪▪▪▪▪▪▪▪▪▪▪▪	Range of concentrations found in organisms from the Regional Copper-Nickel Study Area.
■.	Mean of concentrations in organisms from the Regional Copper-Nickel Study Area
●	Mean of concentrations in organisms from Bob Bay.

SPACE FOR FIGURES 1-47. (Pages 126-172)

FIGURES 1-47

Figures 1 through 47 are in the process of being drafted. An example of these figures has been included to demonstrate the form of these figures.

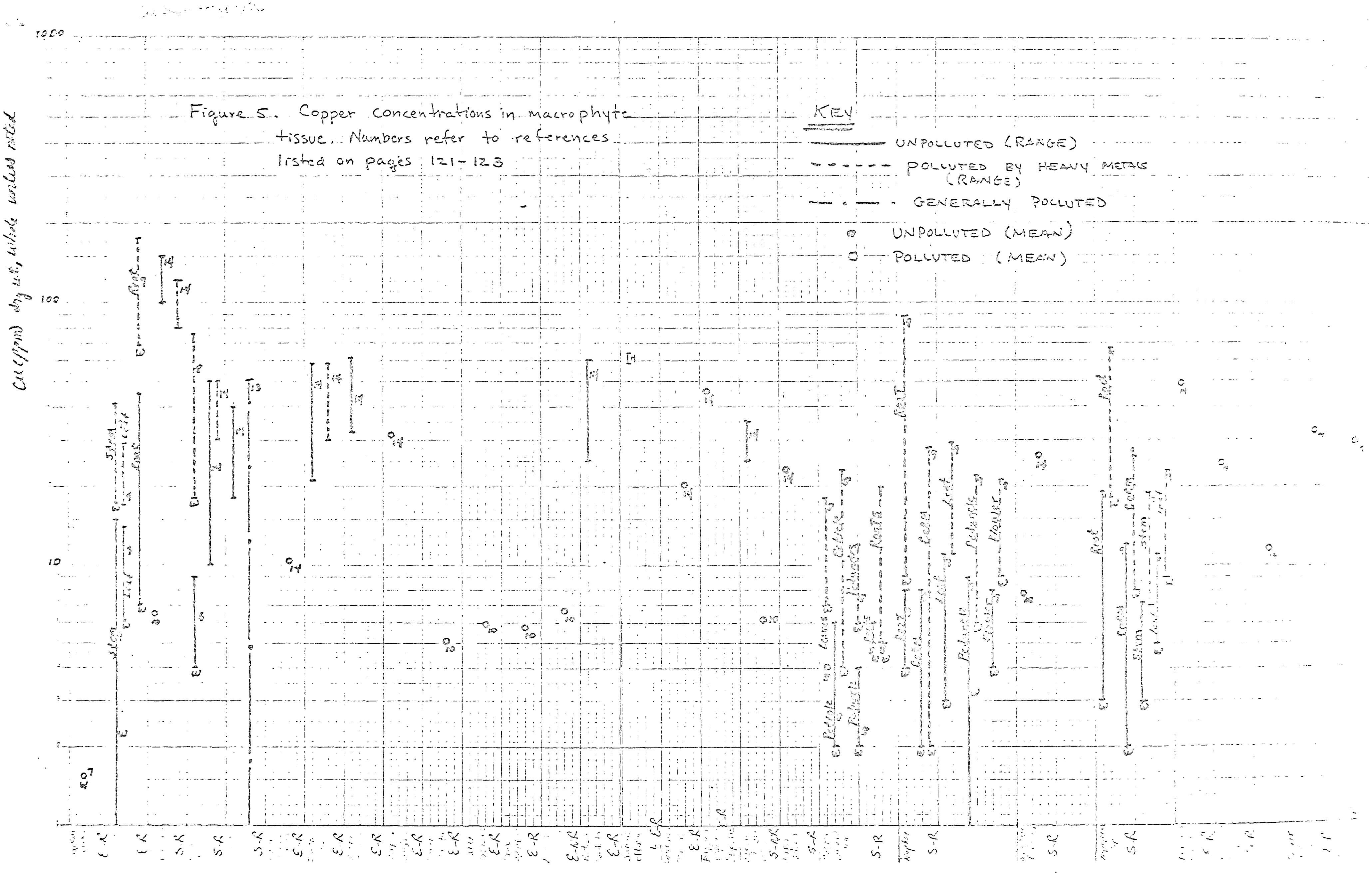

Figure 5. Copper concentrations in macrophyte tissue. Numbers refer to references listed on pages 121-123

Figure 48 Copper in freshwater organisms (See page 124 for explanation of figure)

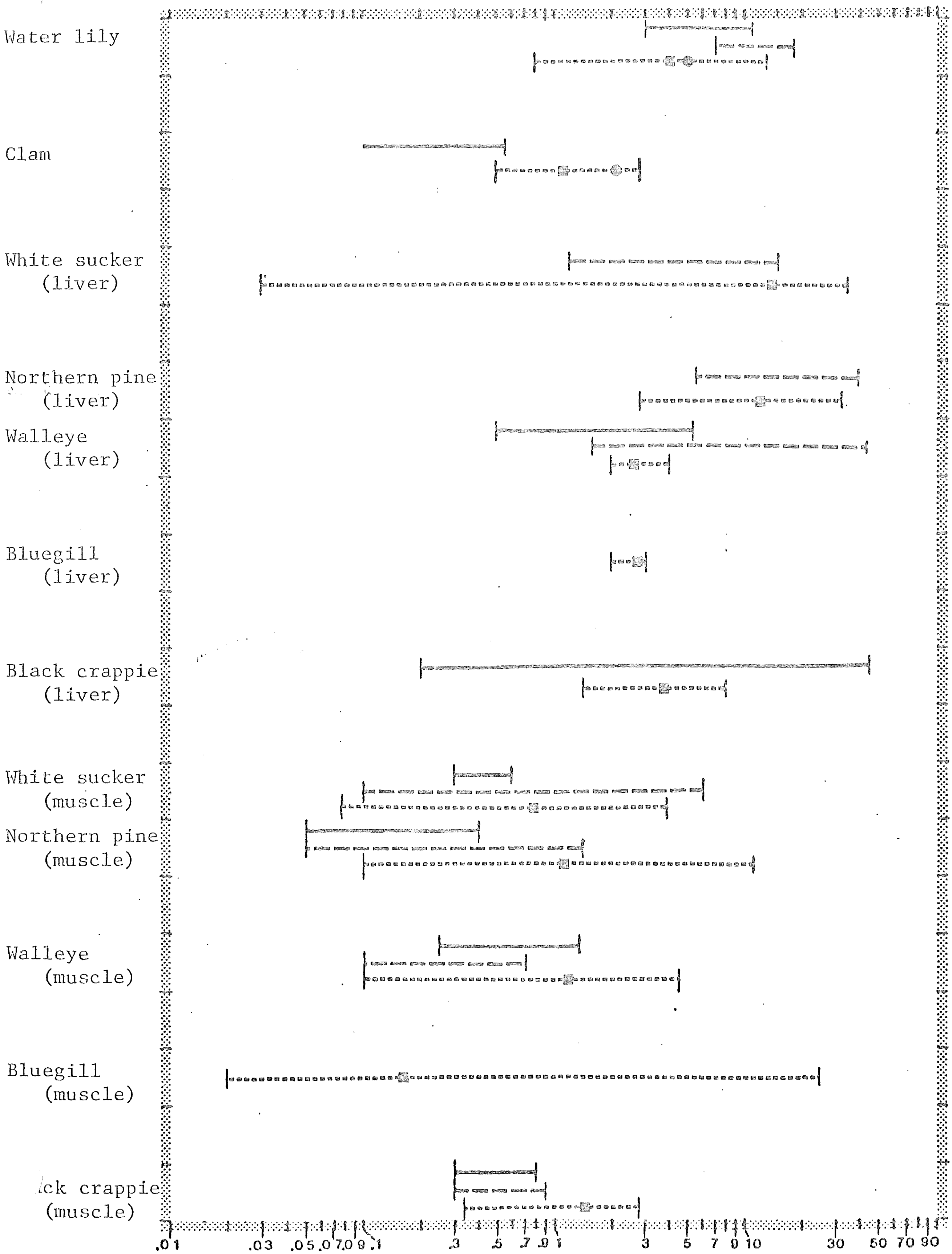

Figure 49 Nickel in freshwater organisms (See page 124 for explanation of figure)

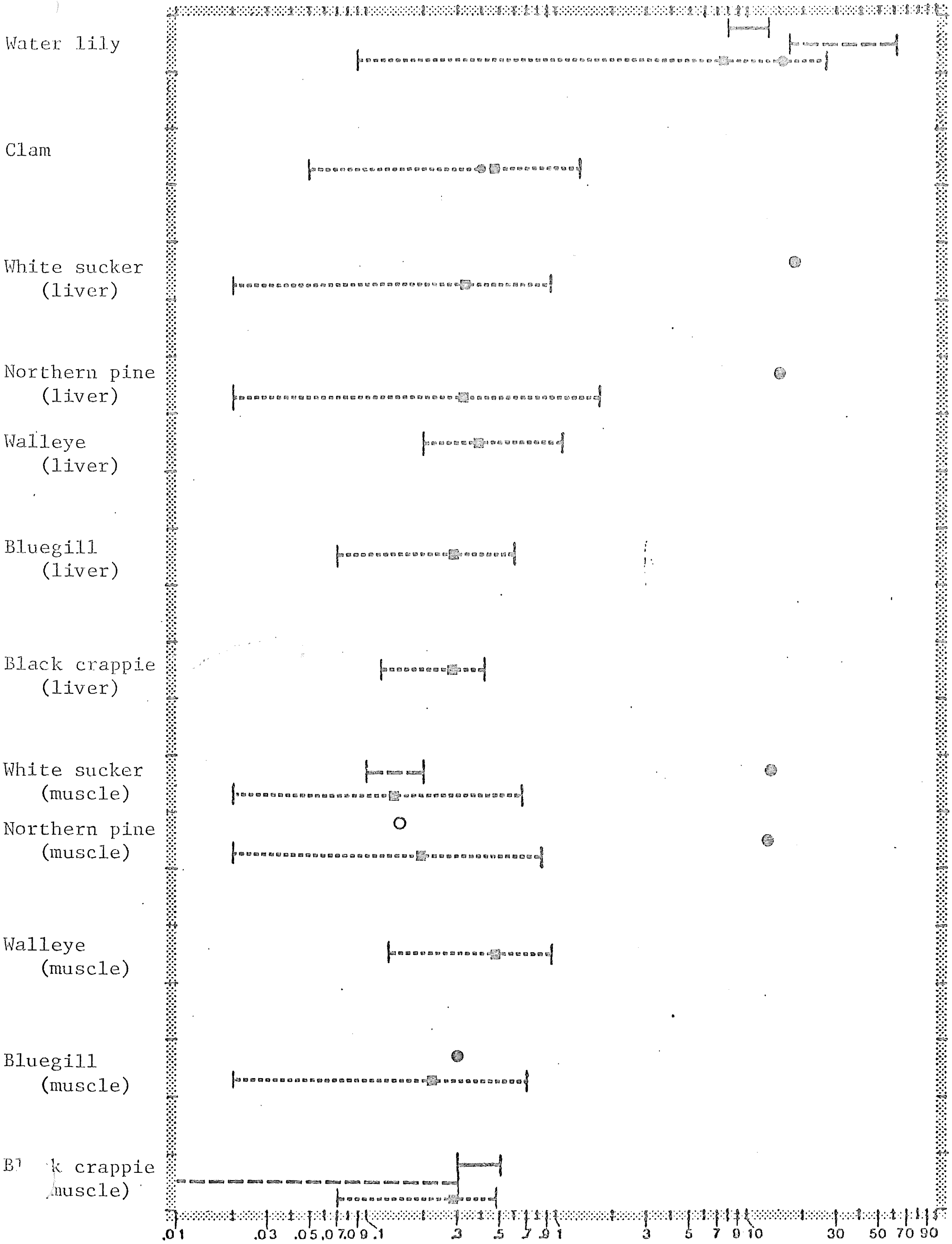

Figure 50 Zinc in freshwater organisms (See page 124 for explanation of figure)

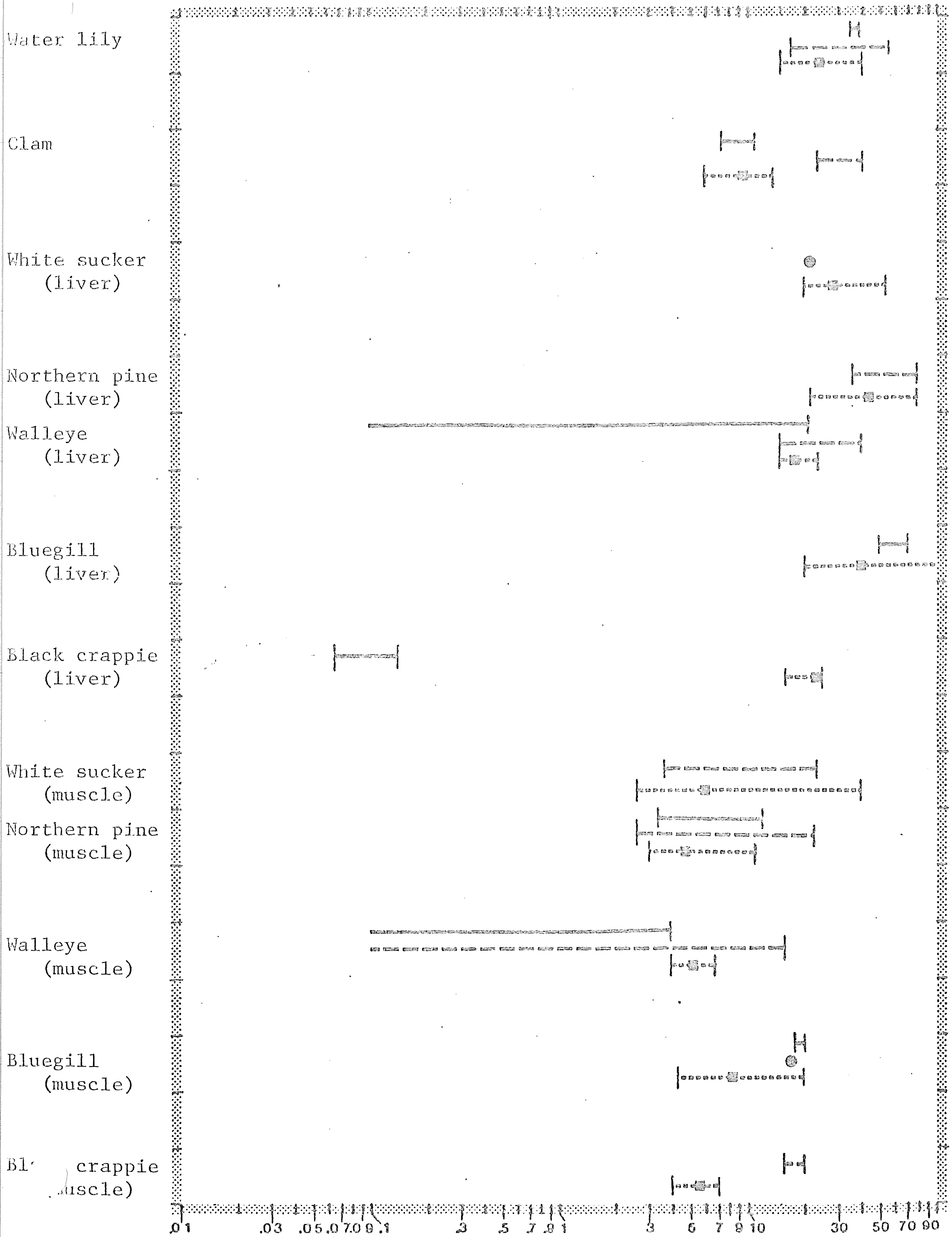

Figure 51 Cadmium in freshwater organisms (See page 124 for explanation of figure)

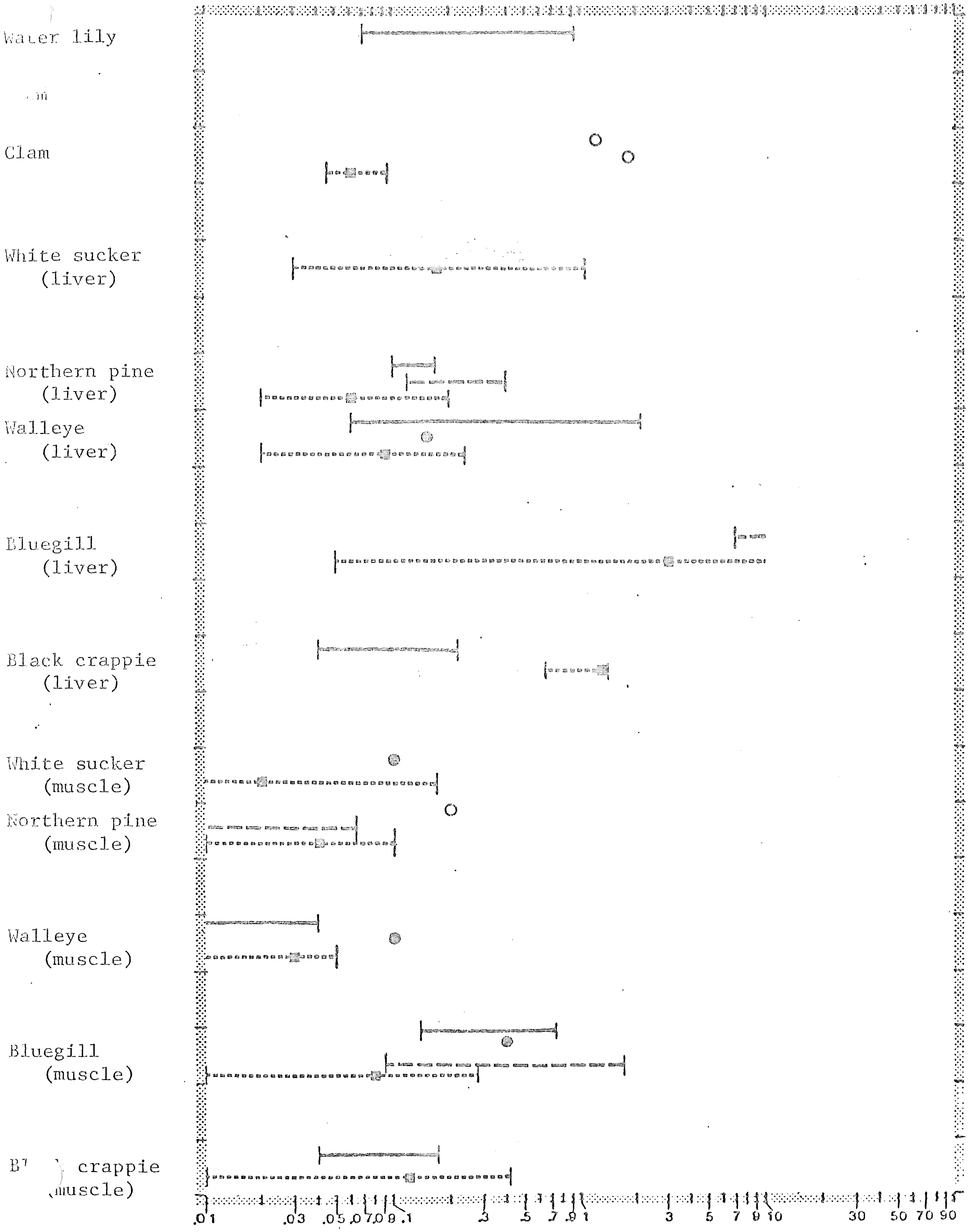

Figure 52 Lead in freshwater organisms (See page 124 for explanation of figure)