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MOBILIZATION OF SELECTED

TRACE METALS IN THE AQUATIC ENVIRONMENT

(Sediment to Water Column and Benthic Invertebrates)

by

KULDIP SINGH BINDRA

B.A.Sc., U.B.C. (1974); M.A.Sc., Univ. of Toronto (1976)

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Kuldip S. Bindra

Department of Civil Engineering

The University of British Columbia
1956 Main Mall
Vancouver, Canada
V6T 1Y3

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ABSTRACT

Laboratory experiments were conducted to determine the processes affecting mobilization of trace metals (Cu, Fe, Mn, Pb and Zn) across the sediment-water and sediment-benthic invertebrate interfaces. The release of trace metals from two contaminated well-characterized sediments was studied under quiescent and agitated conditions. Trace metal release was studied under different conditions of salinity (0-29.5 ^{o}/oo), oxygen (air saturated and nitrogen gas purged) and pH (5, 7, 10). Four groups of benthic invertebrates, namely the opossum shrimp, an amphipod, chironomids, and oligochaetes were exposed to the two sediments for periods up to six weeks. Organisms were analyzed for Cu, Fe, Mn, Pb and Zn to determine whether accumulation occurred.

Rapid agitation confirmed many of the observations made under long term (30 day) quiescent experiments. Under oxic (air saturated) freshwater conditions concentrations of the more toxic metals (Cu, Pb and Zn) were less than 10 μg/l. More Zn (27 μg/l) was released under saline conditions. Iron and Mn were released in high concentrations under anoxic (nitrogen gas purged) conditions. Extreme pH (5,10) resulted in very high concentrations of all metals. Release at pH 10 was attributed to dissolution of humic substances which can bind the metals. Variation in release

could not always be related to the sediment trace metal geochemistry. The sediment organic content and particle size were important in determining trace metal release.

Microcosm studies indicated that total sediment trace metals are not necessarily indicative of levels in benthic invertebrates. The geochemistry of the trace metals as well as the physico-chemical character of the sediment influenced bioavailability. Contaminated sediments were most toxic to the opossum shrimp. Chironomids showed the greatest uptake of all trace metals. Oligochaetes appeared to have the best capability to mobilize and excrete trace metals from their tissue.

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Chapter 1

INTRODUCTION AND LITERATURE REVIEW

I.   INTRODUCTION

A.   General

Effective management of trace metal pollution in the aquatic environment requires a good knowledge of processes responsible for metal mobilization in various components of the environment.

The aquatic environment can be considered as a three component system namely, the water column, sediments, and organisms. The water column salt content may vary from the highly saline marine system through brackish estuaries to the fresh water of most inland lakes and rivers. The sediments can range from highly inorganic sands and gravels to organic ooze often characteristic of highly productive systems. The organisms show a wide array of adaptation to the variety of sediment and water conditions that exist in the aquatic environment. The system is very dynamic with exchange reactions occurring between these three compartments. These exchange reactions are controlled by a wide variety of physical, chemical and biological processes. Mobilization and migration of trace metals is one set of complex processes that can take place between the three components of the system (Figure 1).

Figure 1. Interactions Between Sediments, Water and Benthic Invertebrates.
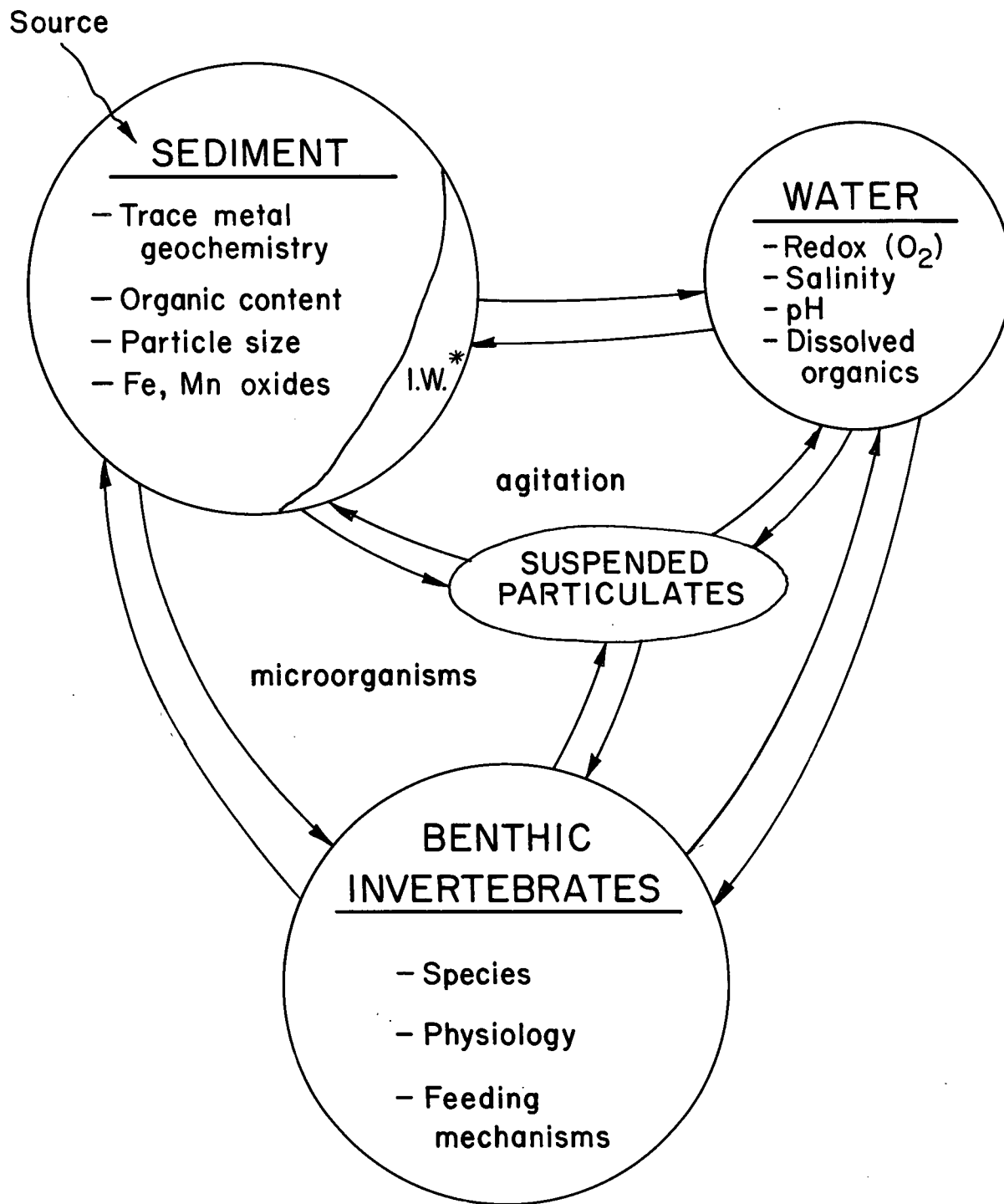
The term "trace metals" may mean different things to different people, but as used here the term refers to a number of metals which are usually found in trace amounts in the aquatic environment. In this study "trace metals" should be considered synonymous to "heavy metals" which include most metals with atomic number greater than 20, but excludes alkali metals, alkaline earths, lanthanides and actinides. The metals most commonly included in the category of heavy metals are silver (Ag), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), titanium (Ti) and zinc (Zn).

Widespread use of metals in modern industrialized and urbanized societies is contributing to trace metal discharges to the aquatic environment from a number of sources such as sewage discharge (with or without industrial waste-waters), dumping of sludges, drainage and discharges from mining sites, metal refining and finishing and numerous other industrial operations, leachates from landfills and by natural processes resulting in washout from atmosphere and contaminated soils.

The potential dangers of uncontrolled pollution of our aquatic environment by trace metals were dramatically demonstrated by a mercury poisoning which occurred during 1960's in Japan (Takeuchi, 1972). To prevent similar events elsewhere and to minimize damage to aquatic ecosystems, the discharge of trace metals must be curtailed at the source.

However, despite considerable efforts at source control, discharges are bound to continue because complete removal of pollutants from effluents is technically difficult and the cost economically prohibitive. Therefore, to minimize the impact of trace metal pollution, a better understanding of trace metal behavior in the aquatic environment is essential.

Trace metals discharged to natural waters are readily removed from the water column and deposited in sediments as a result of low solubility and surficial reactions with suspended materials. The residual water soluble component and the sedimentary deposits may be taken up by aquatic organisms. Dissolved fractions are considered potentially more hazardous because they may directly affect human well-being as a result of contamination of drinking water supplies and fish rearing waters. The sedimentary component may appear to warrant little concern upon preliminary consideration , but on careful investigation this component of the system may prove to be very important. First, trace metals in sediments are often a 1000 times more concentrated than in water. Second, changes in environmental conditions can mobilize trace metals in sediments and make them more available for uptake by organisms.

Some of the environmental factors that may affect release of trace metals associated with sediments to water column are presence and type of complexing compounds, presence or absence of dissolved oxygen, salinity, pH, geochemical and physical characteristics of sediments, and extent of agitation

in both water and sediments. These factors have been studied both in the laboratory and the field, but the results are not conclusive.

Similarly, availability of trace metals to organisms may be affected by a number of factors including physiology of the organisms and characteristics of sediments and water column. Although a myriad of studies have been conducted on uptake of trace metals from water, experiments conducted on mobilization from sediments are rare.

B. Objectives

The objective of this work was to study the trace metal exchange (1) between the sediment and water components and (2) between the sediment and benthic invertebrate components of the aquatic environments (Figure 1).

The work consisted of two distinct parts. In the first part my objective was to investigate the influence of salinity , oxygen, pH, and agitation on the exchange of selected trace metals (Cu, Fe, Mn, Pb and Zn) between sediment and water. Highly contaminated sediments with different organic matter content and particle size distribution were used. The sediments were characterized for trace metal geochemistry to determine the effect of the form of metals on exchange. The effects of both quiescent conditions (static laboratory columns) and agitated conditions (elutriate test) were studied.

In the second part, my objective was to study the effect of organism type, sediment characteristics and trace

metal geochemistry on exchange of the same five metals between sediment and benthic invertebrates. The studies were conducted in microcosms with two contaminated sediments with well characterized properties and trace metal geochemistry.

II. LITERATURE REVIEW

In this section investigations carried out by others on mobilization of trace metals in sediments to water column and benthic invertebrates are reviewed. Metal mobilization to water on one hand, and the benthic organisms, on the other hand, are reviewed separately.

A. Mobilization of Sediment Trace Metals to Water

Trace metals entering natural waters are readily incorporated into sediment deposits. Remobilization of trace metals from sediments may occur under certain environmental conditions. Some of the conditions generally considered to favor remobilization are:

- agitation of sediment deposits
- increase in salt content of water
- changes in redox potential (increase or decrease in dissolved oxygen levels)
- low pH
- presence of organic complexing agents
- microbial action.

Sediment deposits may be agitated as a result of such engineering operations as construction of docks, bridges and outfalls and dredging of navigational channels, off-shore oil exploration, disposal of dredged materials and motion of ships in shallow waters.

Sediments transported by rivers before entering oceans pass through estuaries where the salt content of the

water successively increases from less than 1 $^o/oo$ (parts per thousand) in the river to 36 $^o/oo$ in the ocean. Industrial effluent discharges containing high concentration of dissolved solids may increase salt content of low flow freshwater streams.

Redox potentials in natural waters depend upon dissolved oxygen (D.O.) levels; high D.O. levels indicating high redox potentials and low D.O. levels low redox potentials. Redox changes are often associated with turnover and stratification cycles of natural waters. Deep water sediments are often low in redox potential; discharge of decomposable wastes may also depress redox potential.

Low pH conditions are characteristic of streams in areas affected by mining and ore concentration operations. Natural variation of soil minerals can also affect pH levels in natural waters. Accidental or deliberate discharge of acidic as well as alkaline materials can upset the pH balance of natural waters. Increasing acidity of rain and snow which enter natural waters, due to emissions from industrial sources may also depress pH of natural waters. Poorly buffered waters are particularly susceptible to this stress.

Complexing organic compounds may be leached from soils, produced in aquatic environments or discharged in industrial or domestic effluents. Humic-like substances produced in soils or in aquatic environments by microbial action on dead organic matter of plant or animal origin are an example of naturally produced complexing organic compounds. NTA (nitrilotriacetic acid) used in detergents as a substitute

for phosphates typifies complexing organic compounds discharged in industrial and domestic effluents.

Microbial activity can vary with changes in availability of food and energy sources. For example, environments receiving untreated organic wastes will have a higher microbial activity than an unpolluted environment.

1. Effect of agitation

In the early 1970's over 300,000,000 cubic meters of sediments were dredged annually in the U.S.A. Management of dredging and disposal operations to minimize the impact on the aquatic environment required knowledge of the release/uptake behavior of trace metals and other contaminants. As a result a multimillion dollar research program was launched under the Dredged Material Research Program (DMRP) of the U.S. Corps of Engineers (Engler, 1976).

Under this program, Lee and Plumb (1974) reviewed the existing literature to predict the release of contaminants, including trace metals, and concluded that most trace metals could potentially be mobilized with disturbance of sediments. Wakeman (1977) observed that Cr, Ni, Pb, and Zn were released significantly during the period of a dredging and disposal operation. It was not determined whether the metals were removed from the solid matrix during these operations or were already in solution in pore water.

To assess potential environmental impact of disposal of dredged materials in natural waters the U.S. Environmental Protection Agency (EPA) historically used

dredged material disposal criteria based on the bulk composition of the dredged sediments. Soon it was realized that such a criterion was misleading because environmental impact depends upon only a portion of the total trace metals, the portion which is available to the organisms after leaching from the sediments. Consequently U.S. EPA (1973a) and the U.S. Corps of Engineers (U.S. EPA, 1973b) jointly developed a leaching test under agitation conditions. The test was called the Elutriate Test. Lee et al. (1975) evaluated the performance of the test and recommended the use of the test in predicting the mobilization of trace metals and other contaminants due to resuspension as it occurs in hydraulic dredging operations. The test consists of agitating a sediment-water mixture with compressed air, in a 1:20 ratio for 30 minutes. The agitated mixture is allowed to settle for one hour, and the supernatant decanted, filtered and analyzed for trace metals to determine the increase or decrease in concentrations due to resuspension. Using this test with marine and fresh-water sediments and the associated waters sampled from various geographical locations in the U.S. , Lee et al.(1975) found that Mn is substantially released, Zn was taken up and there was generally no change in concentrations of Cu, Cd, Pb and Fe.

Chen et al. (1976) carried out laboratory investigations to study trace metal mobilization during agitation and during redeposition of the sediments, thus simulating both dredging and dredged material disposal

operations in aquatic environments. Water and sediment samples for their study were obtained from marine and fresh-water environments of the Southern California area. Sediment samples of silty-sand, sandy-silt and silty-clay types were characterized for particle size and geochemical fractions of trace metals. A modified form of the geochemical extraction scheme of Engler et al. (1974) was used for geochemical analysis of the sediments.

Chen et al. (1976) suspended sediment-water mixtures in the ratio of 1:20 in plexiglass columns for 48 hours. Then, they allowed the mixtures to settle. Samples of water were obtained periodically both under suspension and settled conditions and analyzed for trace metals after filtration. Under settled conditions experiments lasted for as long as 120 days.

Under suspension conditions no release of Ag, Cd and Hg was observed by Chen et al. (1976). Concentrations of Cr, Cu and Pb were increased by factors ranging from 3 to 10 over the background seawater levels. Release of Fe, Mn and Zn was even larger. Release of metals from freshwater sediments in seawater was somewhat greater than the release from the marine sediments. Since background levels of trace metals in seawater are generally low and the concentrations of trace metals in seawater after release from sediments were still low, hence the short-term impact of dredging on water quality was considered insignificant.

In the long-term (120 days) experiments of Chen et al. (1976), after sediments were settled, redox conditions

were accurately controlled. Release of trace metals in these quiescent experiments depended upon redox potential. These results will be discussed in a different section of this review.

Windom (1975) reviewed the literature resulting from field studies around dredging operations. His review indicated that the impact of agitation of contaminated sediments on water quality,particularly with respect to trace metals,was minimal. However, the author warned that under certain conditions the release could be substantial and stated that more information is required to determine what might happen when severely contaminated sediments are dredged.

Independent of the DMRP, Rohatgi and Chen (1975) also carried out laboratory experiments which indicated that sediments contaminated with sewage associated solids could in oxic seawater release trace metals on agitation. Sewage solids were kept in suspension in seawater in the presence of air for periods up to 36 days. Release of Cd, Pb, Cu, Ni, Zn and Fe was observed to take place in two-steps, a rapid release followed by a slower long-term release. A similar two step release was also observed for Hg when contaminated organic rich sediments were agitated in situ (Lindberg and Harriss, 1977). In each case the release was attributed to oxidation of organics and subsequent release of the metal ions in the process.

Release of trace metals from disturbed sediments may depend upon a number of other factors (Lu and Chen, 1977; Jones, 1978; Forstner and Wittmann, 1979).

2.   Effect of salinity

In recent years, growing concern has been expressed that discharge of salts in industrial effluents and spring runoff from the highways and snow dumps to freshwater streams and lakes may desorb toxic trace metals (Feick et al., 1972; Hanes et al., 1970; U.S. EPA, 1971; Scott, 1980). Experiments where excessive amounts of sodium chloride and calcium chloride were shaken with freshwater sediments indicated that significant amounts of trace metals like Hg may be released due to desorption with salts (Feick et al., 1972). In these experiments Hg was more easily removed from sandy sediment than from the sediment high in organic matter. Similarly, Holmes et al. (1974) agitated samples of sediment for 30 minutes in 0.5M solution of NaCl. Subsequent analysis of filtered solutions showed a substantial release of Cd and Zn. The extent of metal released in salt solution was in proportion to the amount of the metal leachable from the sediment on agitation for 30 minutes in a solution of 1M hydroxylamine-hydrochloride and 25 percent (v/v) acetic acid.

The potential of release of trace metals bound to sediments is greater in estuarine environments where millions of tons of freshwater sediments transported by rivers are exposed to the saline environment. Although it has been recognized that a complex chemical environment such as an estuary cannot be simulated by simple laboratory experiments involving homogenous reaction kinetics (Turekian, 1977), useful

information about release of trace metals from sediments on
suspension in seawater has been generated.

As part of a major study conducted to estimate
dissolved trace metal flux from rivers to oceans, Kharkar et
al. (1968) carried out adsorption - desorption studies
involving clays, minerals and eight metals (Ag, Sb, Cr, Rb,
Cs, Se, Co and Mo). On the basis of these experiments, the
authors stated that due to desorption from suspended
particulates Co has an additional supply of about twice the
dissolved load, while Ag and Se add only an additional 10
percent more, and Cr and Mo none.

Wagemann et al. (1977) leached suspended and bottom
sediments obtained from the MacKenzie River, N.W.T., Canada,
by mechanically suspending them in Beaufort Seawater for
periods of 2 to 100 hours. No significant release of Cd, Co,
Cr, Pb and Zn from suspended sediment was measured. Iron and
Mn were released to a small but measurable extent. About 50
percent of the copper in seawater was adsorbed by the suspended
sediment. The effect of leaching time was negligible for Fe
but the percent release of Mn significantly increased with time.

Radioactive isotopes of trace metals are chemically
identical to the nonradioactive atoms of the respective metals;
therefore, investigations carried out with labelled metals
are equally important.

Johnson (1966) and Johnson et al. (1967) observed
that although radioisotopes ^{60}Co, ^{65}Zn and ^{54}Mn in the
effluents from the Hanford, Washington, reactor were in ionic

form, they were incorporated into particulates by the time they reached the Columbia River estuary. The authors realized that on mixing with seawater the radioactivity could be released again. Subsequent experiments confirmed the belief; under experimental conditions seawater released some 40 percent of ^{54}Mn, 5 to 15 percent of ^{60}Co and only 1 percent or less of ^{65}Zn. In another study (Robertson et al., 1973) these results were substantiated.

In the above experiments only one to two hour leaching times were allowed. To investigate the effect of longer leaching time, Cutshall et al. (1973) and Evans and Cutshall (1973) provided a leaching time of up to 11 weeks. The percentage of nuclides leached was approximately the same, about 50 percent for ^{54}Mn and very little of ^{65}Zn and ^{60}Co.

Patel et al. (1978) in similar experiments observed that the amount of ^{134}Cs and ^{137}Cs released increased linearly with salinity.

In an estuarine situation, desorption due to increasing salinity is just one of many processes taking place simultaneously (Turekian, 1971). At the river-estuary boundary the three main processes occurring are: (a) desorption of adsorbed trace metals on surfaces of river-borne sediments due to competing cations and the stabilizing effect of complexation with chloride and other anionic species (Kharkar et al., 1968), (b) hydrolysis and coagulation of trace metals due to increasing pH which tends to counterbalance the desorption effect of salinity (Turekian, 1971) and (c) the

increased ionic strength at high salinity induces a

"salting out" effect on the river transported particulates

and those produced in situ (Boyle et al., 1977; Edzwald et

al., 1974). At the estuary-bottom sediment interface,

particulates carrying trace metals accumulate from the

overlying water and , conversely, previously accumulated trace

metals may be released due to chemical and biochemical

reactions. Hydraulic circulation due to tidal cycles is still

another complicating factor (Grieve and Fletcher, 1977).

Consequently, results of estuarine surveys for trace metals

are quite difficult to interpret.

Holmes et al. (1974),during a trace metal survey

in Corpus Christi Bay, Texas, found that Zn and Cd levels

in the sediments were anomalously high and changed signifi-

cantly between the summer and winter seasons. According to

these authors, the metals were precipitated under stagnant

reducing conditions in summer and in winter water currents

increased oxygen levels and as a result trace metals deposited

under low oxygen levels were remobilized due to desorption

and dissolution of precipitates.

A trace metal survey in the Fraser River estuary,

British Columbia, indicated that both dissolved and suspended

loads were increasing in the estuary (Grieve and Fletcher,

1977). The results were explained by adsorption and desorption

taking place simultaneously. Upstream circulation of marine

bottom sediments containing Zn provides the supply of the

metal to correct the apparent imbalance. Thomas and Grill

(1977) also observed increases in dissolved levels for Cu and Zn in the Fraser River estuary and attributed them to desorption at the river-estuary interface.

Graham et al. (1976) investigated Mn in samples obtained from Narragansett Bay, Rhode Island and its surrounding rivers. The results indicated that total Mn was approximately conservative but particulate and dissolved Mn were not. Manganese was dissolving from riverine particulates in tidal reaches of the river at low salinities. In the Bay, dissolved Mn was precipitating, probably due to oxidation at the higher bay water pH.

3. Effect of redox changes

The overall redox condition of sediments has been shown to play an important role in controlling the chemical exchange reactions affecting transport of trace metals across the sediment-water interface. From a literature review Mortimer (1971) concluded that as long as bottom dissolved oxygen concentrations in the Great Lakes remain between 1-2 mg/l, chemical exchange from the sediment deposits may exert a measurable but quantitatively insignificant effect on the chemistry of the water in the lakes. In an earlier work (Mortimer, 1941 and 1942), he found that as dissolved oxygen level fell to analytical zero, redox potential in the surface layer of the sediment as indicated by an electrode also fell. These changes were accompanied by release of sediment trace metals: first Mn, later Fe. In addition to

Mn and Fe release, liberation of ammonia and silicate was also measured. A further decrease in redox potential resulted in microbial reduction of sulphate.

Patrick Jr. et al. (1973) investigated the effect of redox potential and pH conditions on the solubility of strengite, a mineral component of soils and sediments. Suspensions of soil in water containing strengite were incubated for 7 to 10 days at precisely controlled different redox potential[1] (+300 to -250 mV) and pH (5.0 to 8.0) conditions . At the end of the incubation periods the suspensions were extracted with ammonium acetate solutions having the same pH and under the same redox state as the suspensions. Analysis of the extracts indicated that the greatest release of Fe and phosphate occurs under conditions of low oxidation - reduction potential in combination with low pH.

Experiments by Chen et al. (1976) were discussed above. They investigated effects of agitation and redox conditions on trace metal release from geochemically and physically characterized sediments and showed that redox conditions of the water control the exchange reactions, and the geochemistry of sediments plays little or no role. In oxygen deficient conditions they observed a greater release of Fe and Mn. During their quiescent long-term experiments ,

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1. All redox potentials reported in this thesis are
   standard redox potentials (i.e. relative to hydrogen).
   This is the standard practice in the literature.

concentrations of these metals almost reached the ppm[2]

range under reducing conditions.

The effect of redox changes in the water column on
exchange from sediment was studied by Fillos and Swanson
(1974). Water purged with air or nitrogen gas was gently
passed over a layer of river sediment. Concentrations of
nutrients and Fe were measured in the water. Iron and
phosphate were substantially mobilized from sediment when
dissolved oxygen concentration in the water was zero
(achieved by purging with nitrogen gas).

Iron and Mn occur in sediments as hydrous oxide
coatings on particles (Gibbs, 1973). Oxides of Fe and Mn
have long been recognized as scavengers of trace metals
(Jenne, 1968; McKenzie, 1972). Tessier et al. (1980)
conducted a geochemical partitioning study on sediments
obtained from two Quebec rivers and showed that trace metals
originating from anthropogenic sources were bound to Fe and
Mn oxides. Under anoxic conditions the Fe and Mn phase of
sediments becomes unstable and a mobilization of associated
trace metals results (Morgan and Stumm, 1964).

Environmental conditions may change from anoxic
to oxic conditions in stagnant waters such as fjords and
lakes due to turnover during spring and fall (Mortimer, 1942;
Hutchinson, 1957). Dissolved Fe and Mn species undergo
oxidation, hydrolysis and polymerization (Stumm and Morgan,

2. Parts per million. Throughout this thesis 'ppm' when
   applied to water is synonymous to mg/l, but when used for
   solids (sediments or biota) the unit is equivalent to mg/kg
   (or μg/g) on a dry weight basis unless indicated otherwise.

1970; Stumm and Lee, 1960) to form coatings on sediment particles. These freshly formed coatings have strong affinity for other trace metal cations (Jenne, 1968; Means et al., 1978). Thus, the trace metal release may be hindered or completely stopped if redox conditions change from anoxic to partially or fully oxic conditions.

In the above discussion the mobilization of trace metals under the influence of redox changes from sediments would appear to bear a simple relationship to Fe and Mn cycles in the natural environment. However, there are other components which undergo redox changes and in the process affect mobilization of trace metals. Under extremly reducing conditions, sulphate ions are microbially reduced to various sulphide species, H_2S, HS^-, S^{2-} (Bella, 1972). In the presence of sulphides the predicted release of Fe, Mn and associated trace metals may not be observed as metals react with sulphide to form extremely low solubility compounds (Thompson et al., 1975). Spencer and Brewer (1971) in a trace metal survey of the Black Sea observed that in bottom waters Cu and Zn were depleted due to precipitation as insoluble sulphides. However, Fe and Mn concentrations were higher in the bottom anoxic water layer than in the oxic upper layer because sulphides of the reduced forms of these metals are more soluble than the hydroxides and oxides of their oxidized forms. Sulphide deposits of trace metals are stable under anoxic conditions and less soluble sulphides are more stable (Engler and Patrick Jr., 1975).

Presence of organic compounds also affects the mobilization of trace metals from sediments. Pore waters rich in sulphides often have been found to contain trace metal levels far higher than those that can be calculated from metal sulphide solubilities (Presley et al., 1967; Elderfield and Hepworth, 1975; Elderfield et al., 1971). The high concentrations were attributed to formation of soluble complexes with organic compounds. Also under oxic conditions organic compounds play an important role in modifying solubility equilibria of trace metals. Rohatgi and Chen (1975) measured two stage release of trace metals Cd, Cu, Ni, Pb and Zn from sewage-related solids on suspension in seawater under oxic conditions. The first rapid release was attributed to oxidation of readily oxidizable organic matter and the second slow release to oxidation of relatively inert organic matter. A similar two-step release of Hg from organic rich sediments was observed by Lindberg and Harriss (1977). Structurally complex, large molecular weight organic compounds characteristic of anoxic environments are reported to be altered to smaller less complex compounds with less metal binding capacity as a soil or sediment is oxidized (Stevenson and Ardakarni, 1972; Patrick Jr. and Mikkelsen, 1971).

Thus, it appears that under changing redox conditions the fate of trace metals in the aquatic environment is determined by chemical interactions of Fe, Mn, S and organic materials.

4.   pH effects

pH of natural waters may vary considerably; pH values for surface waters may range from 0 to 11 (Krauskopf, 1967). High pH values in surface waters may be caused by natural alkaline compounds from soils in the watershed or by disposal of alkaline industrial wastes, such as products containing caustic soda. Runoff from mining areas and acidic discharges from industrial operations are among the common sources of acidity in natural waters. In recent years, acid rain has been recognized as an important source of acidity of natural waters. In Sweden alone, more than 5000 lakes have pH values below 5 (Babich et al., 1980).

Changes in pH can have an immense effect on solubility of trace metals in water. A number of authors have carried out theoretical calculations for solubilities of selected trace metals (Mann and Deutscher, 1977; Hem,1972; Hem and Durum, 1973; Stumm and Lee,1960). According to solubility - pH curves presented in these references ,trace metals are extremely soluble at pH = 1 or less and in most cases the solubilities rapidly decrease as pH increases towards neutrality. Most trace metals have solubility minima at neutral to slightly alkaline pH values. Under strongly alkaline conditions (pH < 10) the solubilities increase again. This information is obtained from thermodynamic and kinetic data for the trace metals published in the literature and assumes that waters contain only a few selected anionic species such as carbonates, sulphates,

chlorides and hydroxides. In the natural aquatic environment, the presence of particulate and dissolved matter of complex nature may significantly alter the solubility - pH relationships depicted from theoretical calculations (Farrah and Pickering, 1977; Hem, 1972; Payne and Pickering, 1975; Bunzl, 1979; Gupta and Harrison, 1980).

To obtain more meaningful results a limited number of laboratory studies have been conducted using materials obtained from the natural environment. A brief summary of these studies follows:

Stokes and Szokalo (1977) set up laboratory experiments with sediments and water obtained from lakes in the Sudbury area of Ontario. The sediments were contaminated with Cu and Ni believed to be from the metal smelters operating in the area. The purpose of the experiments was to study the effect of dissolved oxygen and microbiological reactions on the release of Cu and Ni associated with the sediments. Sediment cores overlaid with a layer of filtered water were incubated in glass jars under oxic, anoxic, 'live', and 'sterile' conditions. The incubation conditions were established by gently bubbling air (oxic), sealing the glass jars with 'saran wrap' (anoxic), and autoclaving the sediments (sterile). Oxic and anoxic systems with unautoclaved sediments represented 'live' conditions.

Their results showed that Cu and Ni release was substantially greater under aerobic 'live' conditions as compared to that under anaerobic 'live' or 'sterile'

conditions. In each case, the release of the metals
appeared to be related to drop in pH. The drop in pH and
the release of metals was minimum under 'sterile' anaerobic
conditions. Hence, dissolved oxygen (high redox potential)
and microbiological activity seem to favour release of Cu
and Ni by lowering pH of the sediment - water systems. The
authors attributed the greatest pH drop under the live
aerobic conditions to oxidation of sulphur and sulphides in
the sediments to sulphate. This does not mean that redox
potential change was overshadowed by a pH change but that
changes in redox potential could cause a pH change which
was responsible for metal release.

O'Connor and Renn (1964) investigated the
equilibrium relationships between dissolved Zn, suspended
sediment and pH for freshwater systems. Results of their
laboratory studies suggest that the concentration of dissolved
Zn in a natural stream should be inversely proportional to
water pH and the logarithm of suspended solids concentration.

Gambrell et al. (1980) carried out a laboratory
study to determine the effect of different pH and redox
conditions on chemical availability of Hg, Pb and Zn. Mobile
Bay sediments and surface water mixtures were kept in
suspension under precisely controlled pH (5.0, 6.5 and 8.0)
and redox conditions (-150, +50, +250 and +500 mV) for
periods of two weeks. A comparison of trace metal levels in
sediments before and after the two week period indicated that
substantial amounts of Zn were released to water at pH 5 and

oxidizing environmental conditions (+50, +250 and +500 mV). The other two metals were not significantly released, suggesting that trace metal release may also depend on the type of a metal.

Effects of pH on trace metal mobility are more dramatic in low pH natural waters. A study of Adirondack Mountain Lakes (Galloway et al., 1976) showed that trace metals, Al, Fe, Mn and Zn were 10 times higher in water of a lake with pH 4.7 than in the water of another lake with pH of 6.7. At the same time, the top layer of the sediments in the more acidic lake was depleted of trace metals.

Menon et al. (1979) observed that Cd, Cu and Zn levels in South Mosquito Lagoon near Kennedy Space Centre varied seasonally. Trace metal levels in the water were high during the summer months when pH was low; acidity in the water was considered at least partially responsible for the release of trace metals from the bottom sediments.

Sanchez and Lee (1978) noted that, in the epilimnion of Lake Minona, Wisconsin, dissolved Cu levels were inversely related to pH. Increase in dissolved Cu at low pH was attributed to dissolution of Cu carbonate deposits in the sediments of this hardwater lake.

5. Effect of organic complexing agents

Although organic matter normally makes up only 2 to 3 percent of sediments and rarely exceeds a maximum of 20 mg/l in water, it plays an extremely important role in processes affecting trace metals in the aquatic environment. Humic

compounds as principal constituents of organic matter are particularly important.

Mobilization of trace metals by organic substances may occur in a number of ways: (1) Fe and Mn may be reduced to more soluble divalent forms (Hem, 1960; Rawson, 1963), (2) metal ions may form soluble co-ordinate complexes with organic compounds (Rashid and Leonard, 1973; Baker, 1978; Boxma, 1976), (3) the metal ions may mobilize by forming metallo-organic colloids (Hutchinson, 1957; Stumm and Morgan, 1970) and (4) trace metals bound to particulate organic matter may solubilize on break-down of the organics under oxic conditions to simple soluble compounds (Rohatgi and Chen, 1975; and Lindberg and Harriss, 1977).

Kee and Bloomfield (1961) studied the mobilization of a number of trace metals (Cu, Zn, Co, Ni, Mn, Pb, Cr ,Ti, Ga and Mo) from their oxides by decomposing plant materials. Some of the metals (Zn, Cu, Pb, Mn, Fe etc.) were considerably solubilized. Dialysis and pH-stability tests suggested that the metals were in true solution in the form of organic complexes and free ions. Decomposition of plant material was generally accompanied by a decrease in pH; therefore, at least a part of solubilization was due to low pH.

Brockamp (1976) found that Fe and Mn were released from rocks and minerals by the action of organic acids (salicylic acid, citric acid, tannic acid and humic acid) which occur naturally in soils and sediments.

Although the above studies indicate that natural organic compounds can cause considerable mobilization of trace metals from contaminated sediments and soils, discharge of synthetic complexing agents to the aquatic environment via industrial and domestic effluents may make the situation worse. Considerable research effort has been made to investigate the environmental impact of NTA (Nitrilotriacetic acid) from its use in detergents.

Gregor (1972) noted that Pb that had accumulated in sediments as a result of automobile emissions, was released into water containing NTA at concentrations of 2 and 20 mg/l. The release of Pb, at the higher concentration of NTA, was 12 times the American Public Health Service maximum allowable level for drinking water supplies.

Similarly Zitko and Carson (1972) observed that Zn, cupric and ferric ions were released from sediments by NTA even at concentrations as low as 1.0 mg/l. In experiments with different concentrations (0-100 mg/l), they observed that the amount of released metal ions increased with increasing concentration of NTA and leveled off above a certain concentration. In addition, the release depended upon sediment type and hardness of the water used in the study. The release was much greater from the sediments obtained from the Tomogonops River than from those obtained from the Miramichi River. Increased water hardness appeared to suppress the release of the trace metal ions somewhat.

Banat et al. (1974) also measured a high percent release for Cu and Cd and a slight release for Ni from sediments shaken in water containing different concentrations of NTA (1-100 ppm). Sediment samples for this study were obtained from the contaminated parts of the rivers Wupper (Tributary of Rhine) and Elsenz (Tributary of Neckar). The release of Cu and Cd increased with both increasing NTA concentration and shaking time.

As these studies indicate, there is a little doubt that NTA once in the aquatic environment can mobilize trace metals. However, at present a considerable degree of controversy exists with respect to the quantities of NTA discharged to the aquatic environment and its stability once discharged, i.e. , its effective concentration in receiving waters (Stoveland et al., 1980: Shannon et al., 1974).

6. Effect of microbial activity

Three major processes are responsible for mobilization of trace metals through bacterial action: (1) destruction of complex sedimentary organic matter to simple organic compounds which form soluble co-ordinative complexes with the metals, (2) changes in redox potential and pH of the sediment-water systems, and (3) bacterial leaching of metal

sulphides. Literature on the first two processes has already been discussed above, a review of the third process follows.

Although the knowledge that bacteria attack mineral sulphides is relatively new, natural leaching has been occurring for centuries. Presence of Cu in mine drainage was described as early as Roman times (B.C. Research pamphlet). It was only in 1947 that two American scientists, Colmer and Hinkle, showed that acid and iron contained in coal mine drainage are the result of bacterial action on the iron sulphide in the coal seams (B.C. Research pamphlet). As reviewed by Forstner and Wittmann (1979),a group of bacteria, known as Thiobacilli , is capable of oxidizing sulphide to sulphate. The oxidation process supplies energy required by the organisms for their chemoautotrophic growth. These bacteria generally can tolerate acidic conditions; for example, optimum pH for Thiobacillus thiooxidans is approximately 2.0. Oxidation of sulphide to sulphate coupled with resulting low pH provides a mechanism for metal mobilization.

Bacterial leaching is often the cause for high metal concentrations in streams draining mineralized areas. Collins (1973), in a survey of a part of the watershed of Connecticut River, found Cu concentrations as high as 27.8 mg/l. Corbett (1977) measured trace metals in streams in a coal-mining area of West Virginia, and found that concentrations of Fe, Zn, Cu and Cr varied from 0.7 to 650 mg/l. The Coeur d'Alene-Spokane River system in Idaho was shown to contain high levels of

dissolved trace metals (Funk et al., 1977). Zinc concentrations often exceeded 1.0 mg/1. Numerous other examples of high metal concentrations in streams flowing through a mineralized area may be cited (Leland et al.,1978).

Stokes and Szokalo (1977) studied the release of trace metals from sediments contaminated by particulate matter from smelters in the Sudbury area of Ontario. Experiments were conducted under live and sterile conditions. Results from these experiments showed that considerably more Ni and Cu were released from live system than from the sterile system thus suggesting that bacterial action stimulated leaching of trace metals from the sediment.

Bacterial action may also mobilize some trace metals such as Hg by methylation (Wood et al., 1968). This may happen with some other metals as well such as As, Pb and Se (Forstner and Wittmann, 1979).

Still another mechanism for mobilization of trace metals by bacteria in sediments under anaerobic conditions is described by Cline and Upchurch (1973). According to these authors, anaerobic bacterial action on organic matter in sediments produces gases such as CH_4, CO_2, H_2 and H_2S which while migrating upwards through sediment pores could transport metals bound to the associated surface active organic compounds. Szalay and Szilazi (1968) found that by the above mechanism Se and As were migrating upward through the sediment to the water column.

7. Summary

The above review clearly indicates that environmental conditions marked by turbulence, high salinity, low redox potential, low pH, high concentration of dissolved organic compounds and bacterial activity in the presence of metal sulphides favor mobilization of trace metals from sediments to water. However, because of the wide variety of possible physical, chemical and biological conditions in the aquatic environment and complexity of interactions between components of sediment-water systems exchange of trace metals at the sediment-water interface is not fully understood. Factors such as geochemistry of sediment trace metals and sediment characteristics such as particle size and organic matter content may also influence trace metal mobilization processes.

B. Accumulation of Sediment Trace Metals by Benthic Invertebrates

There is a large body of literature dealing with uptake and toxicity of trace metals in solution for a variety of aquatic organisms, but very little has been done on the availability of trace metals in sediments (Leland et al., 1978; Murphy Jr., 1981). Yet, when trace metals enter the aquatic environment they are very rapidly adsorbed and/ or precipitated and become a component of the suspended particulates and ultimately bottom sediments. The concentrations of trace metals in sediments are often a thousand fold greater than values in water. Therefore, a logical pathway of trace metal accumulation is through

organisms that process large amounts of particulate material
or dwell in or near the sediments.

Several studies have been done relating trace metals
in sediments and benthic invertebrates. The following review
is organised on the basis of metal type and organism
classification namely; worms, molluscs, aquatic insects and
other organisms.

1. Copper (Cu)

(a) Worms: The polychaete worm, Nereis
diversicolor , seems to reflect the extent of Cu contamination
of its environment and is proposed by Bryan (1971) as a
suitable indicator organism species for metal contamination
of sediments. Polychaetes sampled from two estuarine
sediments having Cu concentration of 407 and 49 ppm had Cu
contents of 22 and 9 ppm respectively. Further work by Bryan
and Hummerstone (1971) and Luoma and Bryan (no date) further
supports this view. Mathis and Cummings (1973) in a trace
metal survey of water, sediments, fish, clams and worms from
a freshwater system, noted that the highest concentrations of
trace metals were measured in worms, and Cu in these organisms
was even greater than in the sediments.

Luoma and Bryan (no date) observed that Cu in
N. diversicolor was equally related to total Cu and 1N HCl
extractable Cu in sediments. Chapman et al. (1980) stated
that fluctuating levels of Cu in oligochaete tubificids at two
locations in the Fraser River, B.C. and elsewhere

(Bindra and Hall, 1977) reflect local differences in biologically available metal.

Worms ingest large quantities of sediments (Cammen, 1980) to obtain food materials. Observations of Luoma and Bryan (no date) suggest that Cu released from ingested sediments by stomach acids is readily absorbed by the tissue material of the worms. However, the exact route of metal accumulation by tubificids has not been determined (Chapman et al., 1980).

In a laboratory study, Ray et al. (1981) noted that _Nereis virens_ was able to control the levels of Cu in its tissue when exposed to sediments containing 37.4 and 55.5 ppm of total Cu. In the study by Bryan (1974) where a large accumulation of sediment Cu by _Nereis_ was observed, Cu levels in the sediment were greater by several orders of magnitude, indicating that physiological mechanisms controlling Cu levels in the organism were probably overcome. Ash and Lee (1980) , however, believe that such differences in Cu uptake may be due to variations in chemistry of the environment.

Some recent studies show that bacteria (Patrick and Loutit, 1976), algae (Laube et al., 1979) or both (Geesey, 1980) may mobilize Cu and other trace metals from sediments to worms. Bryan and Hummerstone (1971) also presented evidence that a considerable amount of Cu may come from adsorption of dissolved metal in interstitial water of sediments on to the body of the worms.

Preliminary research which led to this thesis project indicated that Cu in the exchangeable and easily reducible phases was important in regulating the metal concentrations in oligochaete worms and some other benthic organisms (Hall and Bindra, 1979).

(b) Molluscs: Molluscs are filter feeders or deposit feeders; therefore, for food supply they depend upon ingestion of sediment or suspended particulate matter. Trace metals associated with ingested sediments may become incorporated in the body tissue of these organisms.

Mussels collected from waters close to major population and industrial centres often contain high concentrations of Cu (Fowler et al., 1974; Fowler and Oregioni, 1976; Anderson, 1977b; Popham et al., 1980). Fowler and Oregioni (1976) attributed the accumulation of Cu by mussels to their feeding habit and their slow uptake and excretion mechanisms. However, Anderson (1977b) believes that greater accumulation in the organisms is due to their ability to extract metals from both water and sediments.

Although the exact route of metal uptake by molluscs is not known, there is sufficient evidence that the organisms accumulate trace metals from sediments. Anderson (1977b) and Mathis and Cummings (1973) determined trace metals, including Cu, in both sediments and clams. Copper levels in the organisms closely reflected the levels in the sediments.

In a laboratory study, Ray et al. (1981) exposed
Macoma balthica to two sediments moderately contaminated
with Cu for a period of 30 days. In each case a significant
amount of the metal was accumulated by the clam. In field
conditions, however, the organism did not accumulate any
Cu (Ray et al., 1979a). These results indicate that factors
such as biochemistry of the organism, physico-chemical
nature of the sediments or environmental conditions like
temperature and salinity of the overlying water may control
the uptake rates.

Pringle et al. (1968) from a literature review
conclude that molluscs appear to accumulate trace metals at
different rates depending on the type and concentrations of
the metal in the environment, temperature, species and
physiological activity of the animal. Physiological controls
of some mollusc species in regulating essential trace metals
like Cu and Zn, however, have been shown to be poor
(Bryan, 1976).

Luoma and Jenne (1975a, 1975b, 1976) have shown
that accumulation of trace metals from sediments depends
upon the nature of geochemical phase(s) to which the metal
is bound. Ray et al. (1981) found that more Cu was
accumulated from the sediment which contained higher levels
of exchangeable and precipitated Cu as indicated by EDTA
extraction of the sediments. Cooke et al. (1979) showed
that availability of trace metals in sediments to edible
cockles is related to the ease with which a metal desorbs

from the sediment.

Larsen (1979) measured Cu levels in hard clams,
Mercenaria mercenaria, caught from two rivers of the Lower
Chesapeake Bay Region. The concentrations in the clam
varied significantly with the age of the organisms. Others
(Romeril, 1979; Boyden, 1974) found a similar age/metal
relationship for Cu in hard clams.

From a statistical analyses of field data obtained
for 18 estuaries, Luoma and Bryan (no date) correlated metal
accumulation by Nereis diversicolor and Scrobicularia plana
with a large number of geochemical and physical factors.
Copper in the clam was related to Ag in the organism. Also
high Cu levels in the clam were observed in the areas where
sediment Fe levels were low and oxygen levels were depressed.
Clams with shells having black hydrogen sulphide stains were
found to contain the highest levels of Cu.

Oysters known to accumulate high concentrations
of Cu appear to reflect levels in the environment. Greig
and Wenzloff (1978) transferred the American Oyster,
Crossostrea virginica , from the relatively unpolluted waters
of North Carolina to seawater and contaminated mud obtained
from Milford Harbour and placed them in an aquarium in the
laboratory. After 22 weeks of exposure to contamination,
the oysters accumulated significant levels of Cu. In an
estuarine environment, concentrations of Cu in oysters
ranged from < 40 ppm for unpolluted areas to 600 ppm for
polluted areas (Watling and Watling, 1976). Ayling's

(1974) data, however, showed that at sediment concentrations of only 50 ppm, oyster tissue levels of Cu may range from 300 to 1300 ppm . Brooks and Rumsby (1965) found that oysters from a sediment containing 100 ppm Cu contained only 40 ppm of the metal. Evidently either availability of Cu in the sediment was limiting or some other controls involving environmental or physiological mechanisms were operative.

(c) Aquatic insects: Anderson (1977a) monitored trace metals including Cu in a number of insects, but did not relate the metal levels in the organisms with those in the sediments.

Namminga and Wilhm (1977) studied the distribution of some trace metals in Skelton Creek, Oklahoma. Concentrations of Cu in chironomids were 10 percent higher than those in the sediments indicating that these organisms can accumulate Cu from the sediments. Bindra and Hall (1977) found even greater accumulation of Cu by these organisms; in field conditions bioconcentration ratios ranged from 1.1 to 4.5. As evidenced by Table 1 (data from Bindra and Hall, 1977) the bioconcentration ratios appear to be depressed by percent fines (<0.25 mm) in the sediments.

(d) Other organisms: In a pollution study of the River Irwell, U.K., Eyres and Pugh-Thomas (1978) investigated the relationship between levels of trace metals in substrate materials and in the tissues of Asellus aquaticus L., a detritivorous water louse, and Erpobdella octoculata (L.), a carnivorous water leech. The substrate

materials were algae scraped from rocks collected from the river bottom. At low substrate concentrations of Cu, the louse accumulated the metal by factors of 2 to 3 above the substrate levels. However, the tissue levels of Cu in the leech did not reach substrate levels,possibly because of blockage of uptake or excretion of the metal by the animals. Copper levels in tissue of both species decreased as the concentration of the metal in the substrate material increased, suggesting that the animals' mechanisms to reduce metal levels in the tissue were more efficient at higher substrate levels.

Copper levels in mud-dwelling Corophium volutator (Crustacea: Amphipoda) were 259 ppm at a coastal site receiving contaminated freshwater drainage (Icely and Nott, 1980). At another site with normal concentrations of Cu, the levels of the metal in the animals were only one-third those of the contaminated site. Hence Cu at the contaminated site was in a readily available form. Also, the investigators found that accumulated Cu in the mud-dweller was concentrated in the electron-dense granular matter in the animal tissue. Walker et al. (1975) propose that trace metals can be detoxified within tissues of animals by incorporation into intracellular granules. Examples of such inclusions in biota have been reviewed by Coombs and George (1978).

Unlike Corophium volutator , the crustacean Crangon septemspinosa, a shrimp, failed to accumulate Cu on exposure to two contaminated sediments in a laboratory

Table I :   Relationship Between Bioconcentration Ratios of
            Copper in Chironomids and Amount of Fines (<0.25 mm)
            in the Sediment (data from Bindra and Hall, 1977)

Bioconcentration Ratio[1]	Percent Fines in the Sediment[2]
4.5	1.5
2.1	4.3
1.9	18.9
1.5	52.8
1.1	56.9

Correlation Coefficient = -0.75

Bioconcentration Ratio = Cu in chironomids/ total Cu in sediments

This ratio is equivalent to concentration factor (van Hook, 1974) when food item(s) of consumer species can be described.

1. From Table 7 of Bindra and Hall, 1977.

2. From Table A4 of Bindra and Hall, 1977 (Sum of particle size fractions 4 and 5).

environment over a 30 day period (Ray et al., 1981).
Consistent with these results, the tissue contents of Cu and
some other metals remained virtually constant in C.
septemspinosa under field conditions. Bryan (1968) also
presented data for a decapod species indicating that some
crustaceans can regulate essential trace metals like Cu and
Zn.

2. Iron (Fe)

(a) Worms: In a laboratory food chain study
using bacteria, tubificids and fish, tubificids concentrated
a number of trace metals including Fe (Patrick and Loutit,
1976). Geesey (1980) demonstrated that worms ingest bacteria
adhering on to sediment particles. These studies suggest
that bacteria may facilitate passage of Fe from sediments to
tubificid worms. In particular, availability of Fe from
sediments rich in organic matter should be greater because
of higher bacterial populations in such sediments. Bindra
and Hall (1977) observed no relation between Fe levels in
aquatic oligochaetes and organic content of sediments. Thus
it appears that as with terrestrial oligochaetes, Fe in the
aquatic oligochaetes is regulated by excretion (Ireland ,
1975).

In a laboratory microcosm experiment with five
benthic animals collected from bay areas of U.S. East Coast, the
lowest Fe accumulation occurred in a polychaete(Guthrie et al.,
1979). Since these animals are deposit feeders one would
expect tissue levels to reflect Fe in the sediments.

Chapman et al.(1980) showed that although Fe concentrations were more than 12500 ppm in sediments the levels in the organisms were only slightly above 1000 ppm . These studies provide further evidence that worms can regulate Fe concentrations in their tissue.

(b) Molluscs: In a marine microcosm consisting of barnacles, crabs, oysters, clams and polychaete, clams contained Fe less than only barnacles (Guthrie et al., 1979). The mean concentration of Fe in the clams, however, was only 1.37 percent of the mean concentration in the sediments. Iron in the hardshell clam, Mercenaria mercenaria , collected from waters of Southampton River, U.K., reflected the Fe levels in sediments and the concentrations dropped along a transect to the sea. In a field study of trace metals in molluscs, Pringle et al. (1968) measured Fe levels in softshell clams, Mya arenaria, ranging from 49.70 to 1710 ppm on a wet weight basis. Pringle et al. also measured Fe levels in oysters obtained from the coastal waters of U.S. The concentrations were: 31-238 ppm in the organisms from the East Coast and 15-91 ppm in those from the West Coast, on a wet weight basis.

Iron has been shown to deposit in mollusc shells as porphyrin-Fe complex (Brooks and Rumsby, 1965).

(c) Aquatic insects: Bindra and Hall (1977) determined Fe levels in chironomid larvae collected from two freshwater streams of the lower Mainland of British Columbia. Associated sediments were characterized for geochemical and physical parameters. Iron levels in the chironomid larvae

appear to be related to the coarseness of the river bed (Table II).

(d) Other organisms: In a marine microcosm consisting of barnacles, crabs, oysters, clams and polychaetes, barnacles accumulated the most Fe and the mean concentration of Fe in this organism was more than one order of magnitude greater than the mean concentrations for the other members of the microcosm (Guthrie et al., 1979).

3. Lead (Pb)

(a) Worms: A number of studies have been conducted relating Pb levels in worms and sediments. In a pollution survey of Illinois River, trace metal levels were measured in water, sediments, fishes, clams and worms (Mathis and Cummings, 1973). Bottom-dwelling worms and clams reflected the sediment Pb levels. Hall and Bindra (1979) also found that in a freshwater environment, Pb burdens of oligochaetes were related to total Pb in the sediments. McNurney et al. (1975) investigated distribution of Pb in the sediments and fauna of rural and urban sections of a mid-western U.S. stream. Lead contents of many organisms were affected evidently by their contact with the bottom sediments. The most striking conclusion of this study, according to the authors, was that oligochaetes which burrow in and ingest sediments had the highest levels of Pb. The concentrations varied widely between urban and rural samples; high concentrations of Pb in urban samples reflected contamination

Table II. Relationship Between Iron in Chironomid Larvae
and Amount of Very Coarse Sand in the Sediment
(data from Bindra and Hall, 1977, pp. 74,84,94,95)

Station	Iron in Chironomids (ppm)	Very Coarse Sand in Sediment (%)
Salmon River at Roberts Road	54	0.3
Salmon River at Springbrook Road	348	0.4
Salmon River at 64th Avenue	678	9.1
Coglan Creek at Otter Road (Salmon River Watershed)	4550	12.5
Still Creek at Grandview Highway (Brunette River Basin)	8790	23.9

Correlation Coefficient = 0.92

Very Coarse Sand is 1-2 mm size

from effluent discharges. Data presented by Packer et al. (1980) appear to show the same trend in Pb concentrations in A. marina and sediments, although the authors report that the correlation in concentrations was statistically insignificant.

Earthworms, terrestrial counterparts of aquatic oligochaetes, have also been found to accumulate Pb from acid soils contaminated by heavy metals (Gish and Christensen, 1973; Ireland, 1975; Van Hook, 1974; Ash and Lee, 1980).

There is ample evidence in the literature that bacteria may play an important role in metal uptake by worms in soils and sediments. Aquatic oligochaetes feed on bacteria adhering to sediment particles (Geesey, 1980; Loutit et al., 1967) and in the process accumulate trace metals concentrated by bacteria from sediment substrates (Loutit et al., 1973). In a food chain study by Patrick and Loutit (1976), oligochaetes were shown to accumulate Pb from ingestion of bacteria grown in metal contaminated media.

Ray et al. (1981) investigated the effect of sediment type on accumulation of Pb by invertebrates. Nereis virens accumulated Pb from only one of the two sediments to which the worms were exposed for 30 days in a laboratory aquarium. The accumulation was observed from the sediment which was slightly coarser, contained slightly less organic carbon and much higher concentration of total and EDTA-extractable Pb.

(b) <u>Molluscs</u>: Accumulation of Pb by molluscs has been the subject of a number of studies. In a mid-western U.S. river, Pb in clams reflected the levels in the bottom sediments (Mathis and Cummings, 1973). Lu et al. (1975) studied the environmental fate and effect of Pb and Cd associated with sewage sludge in terrestrial/aquatic interface ecosystems. Sewage sludge contaminated by metals was applied to model soils draining into model pools. Live animals including a snail (<u>Physa</u>) were placed in the model pools and analyzed for Pb and Cd at the beginning and at the end of the experiments. The results clearly indicated that Pb and Cd added to soils with the sludge were transported to the model pools from where the metals were being readily picked up by the animals. Snails used in this study were also found to accumulate Pb under field conditions (Enk and Mathis, 1977). Anderson (1977b) determined Pb concentrations in tissues of six species of freshwater clams. Lead levels in tissue reflected the concentrations in the environment. Popham et al. (1980) showed that the filter feeder <u>Mytilus</u> <u>edulis</u> is an excellent indicator of Pb pollution; concentrations in the clam collected from Burrard Inlet, Vancouver, declined by two orders of magnitude to background levels only 30 m distance from a source of Pb pollution. In another study, Pb levels in the Pacific oyster, <u>Crossostrea</u> <u>giga</u>, closely paralleled the Pb concentrations in the sediments from which the animals were collected (Ayling, 1974).

Geochemical form of Pb in sediments may affect its

availability to benthic invertebrates. Data from a laboratory study by Ray et al. (1981) shows that equilibrium concentrations of Pb in Macoma balthica exposed to two sediments for a period of 30 days were in exact proportion to the EDTA extractable Pb in the sediments. Luoma and Bryan (1978) related Pb concentrations in the deposit feeding bivalve, Scrobicularia plana, collected from various estuaries in Europe, with metal concentrations in different chemical extracts of sediments. The results indicated that accumulation of Pb in the clam was related to Fe/Pb ratio in the 1N HCl acid extract. Bindra and Hall (1977) determined Pb in M. balthica and sediment samples collected from mud flats along the jetty for the Iona Sewage Treatment Plant outfall in Vancouver, B.C. The concentrations of Pb in the invertebrates and sediment samples were 20.6, 32.0 and 25.3 ppm and 62.4 , 55.2 and 43.7 ppm. respectively. Based on the limited data results do not agree with the control mechanism proposed by Luoma and Bryan (1978). This suggests that bioavailability of Pb in sediments is a complex phenomena and different controls may be operating in different areas, or with different species.

(c) Aquatic insects: A number of studies have been carried out to determine the effect of Pb pollution on aquatic insects. Anderson (1977a) analyzed 35 genera of aquatic macroinvertebrates, including 15 species of insects, collected from the five stations on the Fox River northwest

of Chicago. The stations were affected by urban and
industrial effluents or agricultural runoff. The maximum
Pb concentration of 39 ppm was measured in the Mayfly
nymph, <u>Potamanus</u>. More commonly monitored insects, namely
chironomid larvae, had a Pb value of 30 ppm which is more
than 20 times the mean concentration reported for those
animals collected from the Skeleton Creek,Oklahoma (Namminga
and Wilhm, 1977). The wide difference probably was due to
difference in degree of pollution in the two rivers.

Bindra and Hall (1977) monitored Pb levels in
chironomids collected from two watersheds, urban and rural,
of the Lower Mainland of British Columbia. Animals collected
from the urban watershed had a concentration ratio relative
to sediments of 2.76 while those from the rural watershed
had the ratios in the low range of 0.07 to 0.34. The
difference in accumulation of Pb between the two watersheds
probably was due to different forms of Pb in the sediments.
In the urban sediment 51 percent Pb was in the exchangeable,
organic and sulphur and precipitate phases as compared to
only 11 to 13 percent in the rural sediments. Bissonnette
et al. (1975) also measured concentration ratios over a wide
range of 0.07 to 5.45 for chironomids from four lakes in
western Washington. A similar explanation as in the above
study by Bindra and Hall (1977) may be extended to these
results. However, other factors such as differences in
concentrations of dissolved Pb may also explain the
variation in the observed concentration ratios.

Nehring et al. (1979) investigated the relative availability of dissolved and sediment deposited Pb to aquatic insects. Insects collected from an unpolluted freshwater stream were placed in laboratory aquaria containing either dissolved Pb or Pb bound to sediment substrates. Subsamples of insects were periodically withdrawn and analyzed for Pb. Both dissolved Pb and Pb in the sediment substrate were equally accumulated by the insects. After 100 to 200 hours invertebrates were transferred to clean environment where the tissue Pb levels dropped sharply but appeared to stabilize at higher levels than the original concentrations.

(d) <u>Other organisms</u>: Eyres and Pugh-Thomas (1978) determined Pb, Zn and Cu concentrations in sediment substrate materials and two species of invertebrates: water louse, <u>Asellus</u> <u>aquaticus</u> L., and leech, <u>Erpobdella</u> <u>octoculata</u> (L.) collected from the heavily polluted River Irwell, U.K. Lead concentrations in sediments, louse and leech were in the ranges of 37 - 13905 ppm, trace -595 ppm, and trace -110.9 ppm respectively. A comparison of concentrations in substrate and invertebrates indicated that as Pb increased in substrate, tissue levels of invertebrates also increased but at a lower rate which suggested that either some physico-chemical mechanism is blocking passage of Pb to the animals or the animals are able to excrete the metal actively. Lead levels in leeches collected by Anderson (1977a) from the Fox River near Chicago were quite low (40 ppm) as

compared to concentrations reported by Eyres and Pugh-Thomas (1978).

Four species of crustaceans, <u>Orconectes</u>, <u>Procambrus</u>, <u>Cambrus</u> and <u>Asellus</u> from the Fox River had Pb levels ranging from 16 - 26 ppm and Pb in the fifth crustacean, <u>Gammarus</u>, was below 4 ppm (Anderson, 1977a).

4. <u>Manganese (Mn)</u>

Since manganese is relatively less toxic than Cu, Pb and Zn, fewer studies have been conducted to investigate the effect of this metal on invertebrates.

(a) <u>Worms</u>: Bindra and Hall (1977) in a study of the mechanisms of sediment trace metal uptake by benthic invertebrates, collected a considerable amount of geochemical and physical data for 4 different aquatic environments in the Lower Mainland of British Columbia. Oligochaete worms, however, were found only in the sediments of two freshwater environments, Brunette Basin and Salmon River Basin. In the Brunette Basin, the extent of Mn uptake was related to Mn in the easily reducible phase of the sediments (Bindra and Hall,1977). Combined data for the two watersheds, however, showed no relationship between Mn in oligochaetes and the geochemical phases of the metal in sediments. Some other factors appeared to be responsible for regulation of Mn in the oligochaetes.

A relevant portion of the data from the study by Bindra and Hall is summarized in Table III. Linear

Table III : Manganese Concentrations in Oligochaetes and Sediment Characteristics Which Appear to Affect the Metal Levels in Organisms (data from Bindra and Hall, 1977, Tables A3 and A4).

Stn. No.	Description	Mn in Oligo-chaetes (ppm)	Bioconcent. Ratio	Sediment Characteristics		
				Redox Potential (mV)	Organic Carbon (%)	Sum of Fine Sand & Silt and Clay (%)
1	Brunette R. (Capilano Lumber)	1670	3.21	+3	0.51	21.7
2	Brunette R. (Brunette Ave.)	691	1.36	-38	0.27	13.4
3	Brunette R. (North Road)	3130	4.99	+103	0.23	24.2
4	Stoney Creek (Beaverbrook)	612	1.33	+41	0.27	30.4
5	Stoney Creek (E. Broadway)	435	1.14	+15	0.39	46.0
6	Eagle Creek (Piper Ave.)	1100	0.87	- 7	15.9	90.7
7	Eagle Creek (above Golf course)	384	0.72	-224	15.3	83.9
8	Deer Creek (Glencairon Dr.)	233	0.51	-340	2.1	44.2
9	Still Creek (Lougheed Hwy.)	263	0.56	-434	1.73	61.8
10	Still Creek (Douglas Rd.)	222	0.41	-401	6.04	78.1
11	Still Creek (Wellingdon)	266	0.52	-329	3.86	91.2
12	Still Creek (Gilmore Ave.)	1350	2.74	- 68	0.52	10.9
S- 2	Salmon R. (McKinnon)	476	0.87	-441	0.91	91.4
S- 4	Salmon R. (Rawlison Cres.)	954	1.42	-164	1.23	35.7
S-14	Coglan Creek (Otter Road)	1140	2.09	- 19	0.43	18.9
S-16	Salmon R. (Otter Road)	523	0.69	-105	0.83	38.5
S-18	Salmon R. (Coglan Road)	909	1.07	-110	1.74	73.4

Bioconcentration Ratio = Mn in oligochaetes/total Mn in sediment

Stations 1 to 12 , Brunette Basin ; Stations S-2 to S-18, Salmon River

regression analysis of the data (Table IV) indicates that the most significant correlation for Mn in oligochaetes was with redox potential of sediments and with percent fine material in the sediments when Mn in oligochaetes was expressed as a bioconcentration ratio. Percent organic matter in the sediments also showed some correlation with Mn bioaccumulation in the worms.

The relationship between Mn in oligochaetes and redox potential is further illustrated in Figure 2. It appears that this nonlinear fit is even more significant than the linear fit.

Results of the study by Bindra and Hall seem to be consistent with other literature for Mn in marine worms. Chapman et al. (1980) noted that in the Fraser River, British Columbia, Mn in oligochaetes did not reflect total sediment levels. Similarly, Packer et al. (1980) and Bryan and Hummerstone (1977) observed that Mn in polychaete worms, Arenicola marina and Nereis diversicolor , from coastal and estuarine environments respectively, bore no relationship to Mn in sediments. Manganese in Arenicola marina was below sediment levels, on the average, by a factor of approximately 30 and the factor for Nereis diversicolor was 45. Evidently, variables other than total Mn levels in the sediments determine the metal uptake by worm species. Since redox potentials of mud deposits of deep estuaries and marine areas are usually low, and in light of the findings of Bindra and Hall (1977),it is not surprising that Mn levels are

Table IV : Coefficients of Linear Correlations (r) Between
Manganese Levels in Oligochaetes and Their
Habitat-Related Parameters (data from Bindra and
Hall, 1977, Table III of this thesis)

	Redox Potential (mV)	Organic carbon in Sediment (%)	Sum of Fine Sand & Silt and Clay(%)
Mn in Oligo-chaetes	0.653[1] (n=17)	-0.481[2] (n=15)	-0.394[3] (n=17)
Bioconcent-ration Ratio	0.641[1] (n=17)	-0.403[3] (n=15)	-0.616[1] (n=17)

1. $0.01 > P > 0.001$
2. $0.05 > P > 0.01$
3. $0.2 > P > 0.1$

Figure 2. Relationship Between Mn in Oligochaetes and Redox Potential of Sediment (data from Bindra and Hall, 1977).
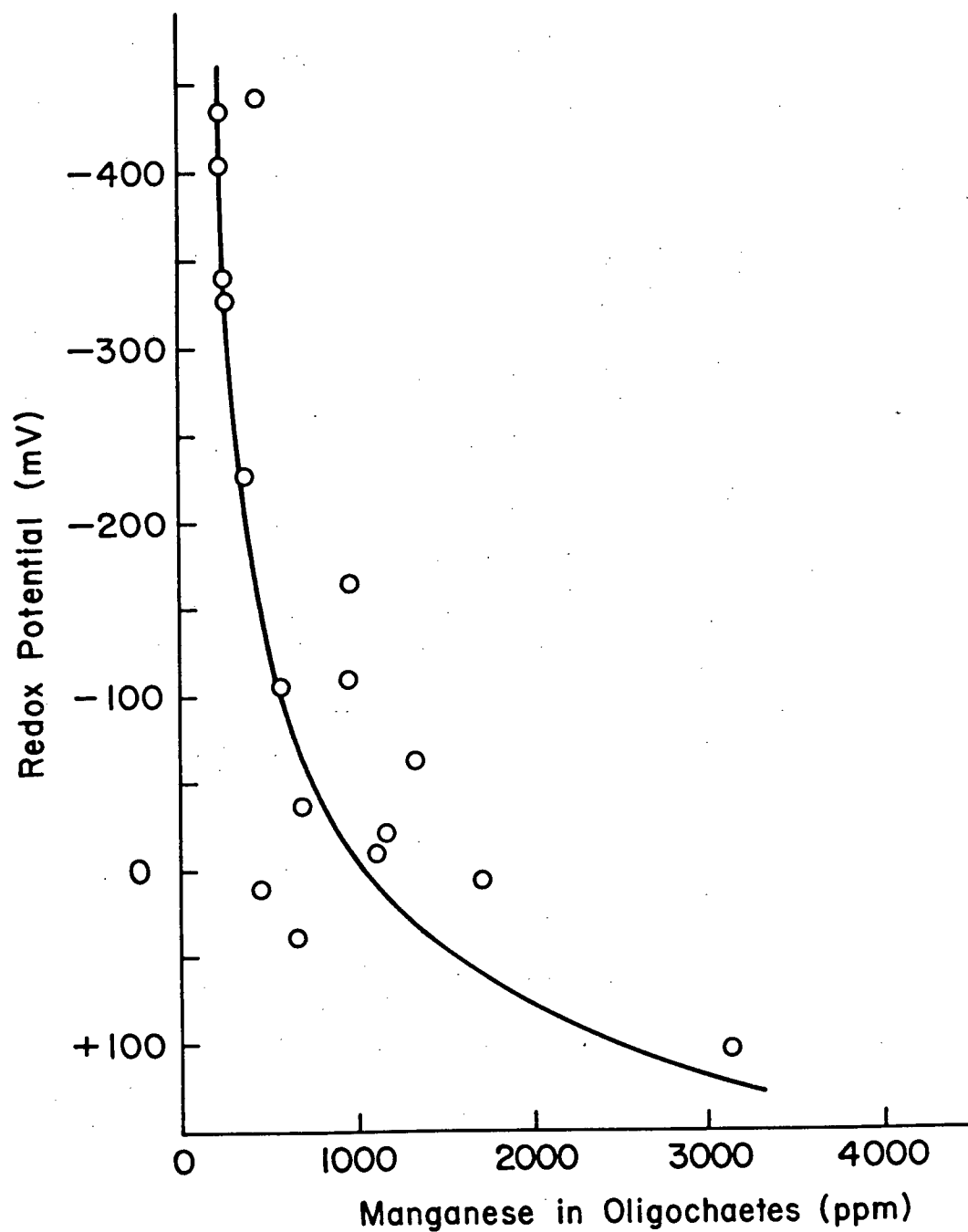
depressed in the worms.

Patrick and Loutit (1976) showed that bacteria
may mediate transfer of Mn from sediments to tubificids. Thus,
it would appear that the greater uptake of Mn by oligochaetes
under higher redox potential observed by Bindra and Hall
(1977) and as shown in Figure 2 may have been due to greater
supply of Mn containing bacterial mass under aerobic
(high redox) conditions.

(b) Molluscs: Feeding habits of molluscs seem to
affect the Mn levels in the organisms. Results of several
studies suggest that deposit feeders have higher tissue Mn
levels than the filter feeders. Also, the literature
indicates that molluscs collected from marine environments
accumulated only a small fraction of the total Mn in the
sediments.

In a biomagnification study by Guthrie et al.(1979)
Mn levels in oysters and clams from the Galveston area of
Texas were 1.4 and 7.6 ppm, respectively, while the sediment
had a Mn concentration of 114 ppm. Bryan and Hummerstone
(1977) also observed a similar Mn distribution pattern.
Manganese levels in deposit feeder bivalves, Scrobicularia
plana and Macoma balthica were approximately 1.5 - 3 times
greater than in filter feeders, Cerastoderma edule and
Mytilus edulis. Filter feeders as well as deposit feeders,
however, accumulated only a small fraction (0.034 - 0.10)
of total Mn in the sediments.

Differences in Mn accumulation due to feeding habits

are also evident from the data presented by Pringle et al. (1968). Oysters (Crassostrea virginica and C. gigas) and softshell clams (Mercenaria mercenaria and Mya arenaria) collected from the U.S. East Coast and some from the West Coast contained average Mn levels of 4.3 ppm and 6.7 ppm respectively. The higher levels in clams were probably due to their having greater contact with the sediments and being deposit feeders. A deposit feeder, Macoma balthica, collected from 3 stations in the Sturgeon Bank area off the Iona Sewage Treatment Plant outfall, Vancouver, British Columbia had Mn levels up to 209 ppm (Bindra and Hall, 1977).

Freshwater Pelecypod molluscs (clams and mussels) are reported to have very high affinity for Mn, Zn and Al (Forester, 1980). A review by Forester indicated that Mn levels for freshwater mussels ranged from 500 - 3500 ppm. Although the accumulation was compared to water concentrations, Mn levels in sediments were not reported.

(c) Aquatic insects: Bindra and Hall (1977) presented data for Mn in chironomid larvae and sediments collected from a station on an urban creek and 4 stations on a rural river system. The bioconcentration ratio (organism/sediment) for the urban station was 2.84 as compared to 0.034 - 0.171 for the rural stations. These results suggest that Mn from urban pollution is readily bioavailable. Barica et al. (1973) found that synthetic chelating agents released sediment Mn and some other trace metals to water but had no effect on uptake of Mn by chironomids. Thus

it appears that the insects receive Mn mainly from benthic food sources.

(d) <u>Other organisms</u>: In a marine microcosm consisting of barnacles, crabs, oysters, clams and polychaetes, crabs contained the lowest levels of Mn (Guthrie et al.,1979). Crabs appear to control Mn levels in tissue. A freshwater crustacean crayfish, growing in a stream receiving mine tailings also had relatively low levels of Mn as compared to tadpoles (Gale et al., 1973). Manganese levels in tadpoles dropped rapidly with distance from the tailings pond, reflecting metal levels in the environment.

5. <u>Zinc (Zn)</u>

(a) <u>Worms</u>: Results of studies on Zn accumulation in worms are often contradictory. Dean (1974) in a laboratory study using a radioisotope of Zn, ^{65}Zn, showed that tubificid worms do not accumulate Zn when it is bound to sediments whereas Zn in solution may be readily picked up by the worms. Yet, Ray et al. (1979b) report that Zn in <u>Nereis</u> <u>virens</u> remained constant when exposed to water containing 1.0 mg Zn/l. Guthrie et al. (1979) attribute a high concentration of Zn in polychaetes from a marine microcosm to its ability to accumulate Zn from both sediment and water. Bindra and Hall (1977) (Table V) and others (Bryan, 1976; Packer et al.,1980) presented data which show that under field conditions Zn in worms may accumulate many times above the sediment levels. Ray et al. (1981) on the contrary failed to observe any change in concentration of Zn in <u>Nereis</u> <u>virens</u> exposed to

Table V :   Bioconcentration Ratios of Zinc in Oligochaetes
from Three Watersheds of the Lower Mainland of
British Columbia (adapted from Bindra and Hall,
1977, p. 40)[1]

Station No.	Bioconcentration Ratio (organisms/sediment)
1	8.53
2	6.06
3	7.91
4	7.95
5	4.88
6	3.32
7	1.85
8	1.28
9	3.06
10	1.15
11	1.65
12	7.66
S- 2	2.86
S- 4	1.66
S-14	9.46
S-16	4.02
S-18	4.21
A	0.20
B	0.56
C	1.27

1.   Three Watersheds:
   (a) Brunette River Basin - stations 1-12.
   (b) Salmon River Basin - stations S-2 to S-18.
   (c) Ladner Side Channel - stations A,B and C.

two contaminated sediments, in laboratory aquaria, for 30 days. Obviously, mechanisms for Zn accumulation in the worms from their environment are quite complex.

In a number of field studies (Bryan, 1976; Bryan and Hummerstone,1977; Ray et al., 1979a; Chapman et al.,1980) correlation between Zn in sediments and Zn in worms burrowing in the sediments was found to be insignificant. In these studies, lack of relationship between Zn in sediments and organisms was attributed to either the ability of organisms to control metals in their tissue (Bryan, 1976; Bryan and Hummerstone, 1977) or variability in availability of Zn in the sediments (Chapman et al., 1980).

Hall and Bindra (1979) studied the distribution of trace metals in various geochemical phases of sediments and in the burrowing oligochaete worms, collected from various watersheds of the Lower Mainland of British Columbia. Sediments were characterized for a number of chemical and physical parameters such as pH, redox potential, percent organic and inorganic carbon, and particle size distribution. No single parameter appeared to control Zn in the worms.

Patrick and Loutit (1976) suggested that Zn associated with aquatic sediments may be concentrated by bacteria and passed on to tubificid worms which ingest bacteria coated sediments for food (Geesey, 1980).

Although many such mechanisms have been proposed, actual route of metal uptake by worms has not been determined (Chapman et al., 1980).

(b) <u>Molluscs</u>: Freshwater clams and mussels are known to have a high affinity for Zn (Forester, 1980). Mathis and Cummings (1973) determined a number of trace metals in components of a freshwater ecosystem (sediments, water, worms, clams and fishes). Maximum concentrations of Zn among the biota occurred in clams and most closely reflected sediment levels. Anderson (1977b) reported Zn concentrations in six species of freshwater clam and sediments collected from the Fox River near Chicago. Zinc levels in clams were greater than those for the sediments. Distribution of Zn in various organs of two species of clam (<u>Anodonta</u> <u>marginata</u> and <u>Lasmigona</u> <u>complanata</u>) indicated maximum concentrations in gills and viscera suggesting that Zn uptake is mainly through food intake.

Zinc levels in molluscs in at least three estuaries have been found to decline with distance from the mouths of the estuaries. Bryan and Hummerstone (1977) in a trace metal survey of the Looe Estuary, U.K., observed that Zn concentrations in most molluscan species and sediments dropped toward the sea. Larsen (1979) and Romeril (1979) also found that Zn levels in the hardshell clam, <u>Mercenaria</u> <u>mercenaria</u>, fell as salinity increased in the James River and Southampton waters respectively. Similar trends in Zn concentrations have been measured for sediments (Romeril, 1979; Chapman et al., 1980). Popham et al. (1980) showed that mussels are quite sensitive to metal pollution in the environment.

Zinc accumulation among molluscan species may vary due to differences in physiological metal requirements of the animals (Pringle et al.,1968). A trace metal survey of shell fish along the U.S. Atlantic Coast and the Pacific Coast (Washington State) found that Zn in the organisms obtained from the Atlantic Coast varied from approximately 10-40 ppm for hardshell and softshell clams to values of 180-4100 ppm for the Eastern oyster. Zinc concentrations in the Pacific oysters were lower by a factor of 10. Zinc concentrations in the organisms also depended on degree of pollution in the coastal areas and water temperature.

Pacific oysters (Crassostrea giga) caught from 15 stations along the Tamar River, Tasmania, contained Zn levels in proportion to and exceeding those in the sediments (Ayling, 1974). This suggests that animal controls based on physiological needs may be overwhelmed if concentrations in the sediments are high enough. Results of a laboratory study by Ray et al. (1981) support this hypothesis. The clam, Macoma balthica, exposed to two sediments varying widely in Zn contamination accumulated Zn only from the sediment which contained very high levels of the metal.

Also, it has been shown that accumulation of trace metals by bivalve clams may depend upon the geochemical form of the metals (Luoma and Jenne, 1975a,b). Luoma and Jenne (1975b) studied the uptake of radiolabelled Ag, Cd, Co and Zn by the deposit feeding clam M. balthica. They coprecipitated the metals with amorphous Pb and Mn oxides and

synthetic calcite or adsorbed them to biogenic carbonates
or detrital organics and then M. balthica was allowed to feed
on these materials. At the end of the experiment , tissue
levels of metals in the bivalve were determined. The uptake
of Zn was high from biogenic carbonates, but very little
accumulation of the metal took place from Pb and Mn oxides.
Zinc bound to biogenic carbonate was readily desorbed by
seawater. Thus, the ability of a clam to assimilate Zn was
related to the weakness of bonding between Zn ions and the
sediment particles.

Luoma and Jenne (1976) compared the leachability
of Zn (also Ag, Cd and Co) from model sediments and
accumulation of the metal by M. balthica . Accumulation of
Zn by the clam from various sediments was best related to
amount of metal extracted by 1N ammonium acetate or 1N sodium
hydroxide plus EDTA. The amount of Zn removed from sediments
by weak acids (0.1N hydrochloric acid; 25% acetic acid),
reducing agents (1N hydroxylamine hydrochloride in 0.01N
nitric acid; sodium dithionite plus citrate) or oxidizing
agents (3% hydrogen peroxide plus citrate) showed a poor
relation to the metal accumulated by the clam.

Luoma and Bryan (1979) investigated   availability
of sediment-bound Zn to two species of clam (M. balthica and
Scrobicularia plana) under field conditions. Sediments and
organisms were collected from two separate study areas. One
study area was San Francisco Bay where M. balthica and
sediments were sampled. The second study area was southwest

England in which S. plana and sediments were collected from 17 estuaries. Zinc concentration ratios between the clams and sediments were regressed against Fe, Mn and Zn in various chemical extracts and sediment characteristics such as organic and inorganic carbon content and combinations of these. The regression analyses indicated that physiochemical form of Zn in the sediments affected the availability of the metal to the clam. Significant correlation was obtained between ammonium acetate soluble Zn in sediments and Zn in Scrobicularia. Other correlations indicated that the presence of high levels of amorphous Fe and Mn oxides or humic substances in sediments enhances availability of sediment-bound Zn to clam species.

(c) Aquatic insects: Namminga and Wilhm (1977) related trace metal levels in chironomids and sediments collected from Skeleton Creek, Oklahoma. The mean concentration of Zn in the organisms was 57 ppm, 3.6 times the mean concentration in the sediments. Bindra and Hall (1977) also determined Zn levels in chironomid larvae collected from the Brunette River and Salmon River basins in the Lower Mainland of British Columbia. The metal levels in the chironomids were compared to Zn concentrations in various chemical extracts of sediments and physical and chemical characteristics of sediments such as organic and inorganic carbon, pH, redox potential, particle size fractions. No relationships were observed. Bioconcentration ratios between organisms and sediments differed considerably between grossly polluted

Still Creek and only slightly polluted rural Salmon River
(Table VI).

(d) <u>Other organisms</u>: In a trace metal study of
River Irwell, U.K., Eyres and Pugh-Thomas (1978) found that
as substrate Zn levels increased, tissue levels in <u>Asellus</u>
<u>aquaticus</u> and <u>Erpobdella octoculata</u> decreased. The authors
admitted although the exact mechanisms of trace metal
control in the animals were not known, two possibilities
existed: (1) the animals were able to block entry of the
metal into their bodies or (2) the metals entering the animal
bodies were effectively removed through animal excretions.
Similar metal controls were also operative in <u>Crangon</u>
<u>septemponosa</u> when it failed to accumulate Zn from two
contaminated sediments to which the shrimp was exposed in a
laboratory for a period of 30 days (Ray et al., 1981).

6. Summary

Trace metal levels in benthic organisms do not
always reflect the concentrations in sediments. This
suggests that other factors help regulate organism trace
metal levels. Although the exact nature of these controls is
not known, much speculation exists. Among the suggested
controls are the ability of the organisms to block uptake or
effectively excrete the metals entering the animal body, and
limited bioavailability of the total metal in the sediments.
The latter has been recognized only recently. It is believed
that the geochemical form of the metal in sediments may

Table VI :   Comparison of Bioconcentration Ratios of Zinc in
             Chironomids from Two Watersheds, Lower Mainland,
             British Columbia (from Bindra and Hall, 1977, p.40)

Watershed	Station	Bioconcentration Ratio	Comments
Still Creek	Grandview Hwy.	8.16	Urban
Salmon River	Springbrook Rd.	3.76	Rural
Salmon River	64th Avenue	3.34	Rural
Salmon River	Coglan Creek at Otter Rd.	2.95	Rural
Salmon River	Roberts Rd.	2.48	Rural

Bioconcentration Ratio = Zn in chironomids/ total Zn in sediment

determine its potential availability. Not many studies have been conducted to evaluate the relationship between biological uptake and geochemistry of trace metals.

Chapter 2

MATERIALS AND METHODS

I.   MATERIALS AND METHODS FOR EXCHANGE BETWEEN SEDIMENTS

AND WATER

Laboratory experiments were set up to determine
the effects of oxygen , pH, salinity, sediment type (particle
size and organic content) and agitation on the exchange of
trace metals between sediments and water. Vertical plexi-
glass cylinders containing 5 cm of sediment under a 100 cm
column of water were used to simulate natural quiescent
conditions for exchange. The variables studied in these
static columns included oxygen, pH, salinity and sediment
type. Concentrations of trace metals Cu, Fe, Pb, Zn and
sometimes Mn were monitored in the water column above the
sediment for approximately 5 weeks or until equilibrium
conditions were established. Elutriate tests (see P. 8)
were performed to investigate the effects of agitation in
combination with oxygen, pH, salinity, and sediment type on
trace metal exchange.

All column studies and elutriate tests were
performed on two sediments differing in particle size and
organic matter content.

A. Column Studies

1. Sampling

(a) Sediment: Sediments for all exchange studies were obtained from the two previously established stations in Still Creek (Bindra and Hall, 1977), station No. 11 (at Willingdon Avenue) and No. 12 (at Gilmore Avenue) in the Brunette Basin in Burnaby, B.C. The criterion for their selection was that sediments at both stations contained high levels of exchangeable trace metals and differed significantly in particle size and organic matter content. The sediment collected at Willingdon Avenue was mainly silt and clay and relatively high in organic matter content. In contrast, the sediment collected at Gilmore Avenue was coarse (sandy) and relatively low in organic content.

For column studies the sediments were collected on two occasions:
(1) 23 Dec. 1977 (used in oxic, anoxic, salinity columns and low organic-pH columns)
(2) 19 April 1978 (used in high organic-pH columns, also used in elutriate tests described later)

Approximately 20 liters of sediment were collected on each occasion with an aluminum pot. The sediments were immediately sieved through a coarse (2 mm) plastic sieve to remove coarse materials and placed in plastic bags flushed with nitrogen and transported to the laboratory in iced coolers. A small portion of each sediment was used for geochemical fractionation and for determination of organic matter, particle size and percent dry weight. The remaining sediments were placed in plastic bags and stored for periods up to 115 days in a freezer until needed. Although storing

of sediments even under freezing conditions can affect geo-
chemical distribution of metals, for comparison of results it
is important that all similar experiments be performed with the
same sediment.

(b) Water: Freshwater for the column studies
was obtained at the same Still Creek stations as the sediments
just prior to setting up the columns. Seawater for salinity
changes was obtained from the seawater tap at the Pacific
Environmental Institute (PEI) in West Vancouver which takes
seawater several hundred meters offshore and several meters
deep. All water was collected in clean plastic containers
and stored at 4 °C until used.

2. Construction of columns

Four plexiglass columns 122 cm high, 30.5 cm OD
and 29.2 cm ID with plexiglass bottoms and tops were
constructed in the Civil Engineering Workshop. A glass tube
with a gas dispersion tube at its lower end was suspended in
each column. The columns were fitted with several sampling
ports covered with rubber cups filled with silicon sealant.
Columns were supported on 45 cm wooden bases to facilitate
sampling and cleaning of columns. A schematic of a column
is shown in Figure 3.

Three similar columns of smaller diameter
(14 cm OD) were used to study the effect of pH on trace
metal dynamics.

3. Setup of columns, operation and sampling

Frozen sediment with a wet volume of approximately
3.5 liters was placed into a column and immediately overlain

Figure 3. Sketch of a Column

6 mm plastic tubing to source of compressed air or nitrogen gas

vent hole

plexiglass column

30.5 O.D.
29.3 I.D.

sampling port

15 cm
15 cm
15 cm
7.5 cm
7.5 cm

122.0 cm

wooden support

45.8 cm

6 mm

clamp

rubber cup

9 mm

6 mm

silicon sealant

2.5 cm

column wall
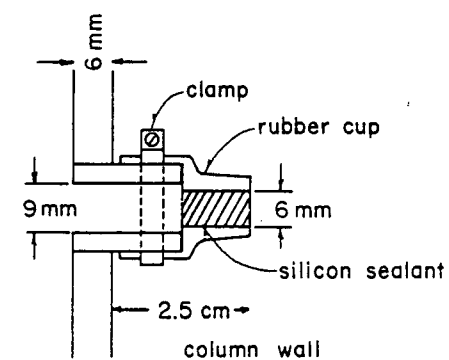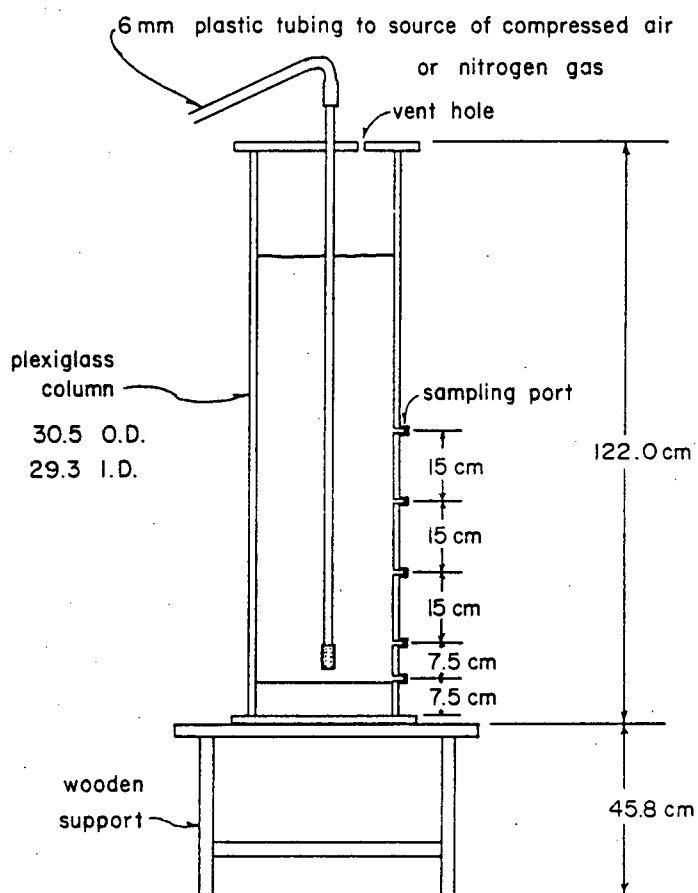
SAMPLING PORT

with 70 liters of freshwater using a siphon arrangement to give a sediment to water ratio of 1:20. Compressed air from the laboratory outlet was connected to the glass tubes and allowed to purge the water column with the dispersion head 10 cm above the sediment to prevent sediment resuspension. To generate anoxic conditions, compressed nitrogen gas, passing through a pyrogallol and deionized water cleaning train, was used to replace the air. For anoxic runs, freshwater was purged with nitrogen before siphoning into the columns. After 24 hours equilibration, sampling began through the lower port using plastic syringes to obtain 250 ml of sample. The samples were filtered through 0.45 μm membrane filters,[1] acidified and stored for subsequent analysis. The filters retaining suspended solids were stored in clean petri dishes prior to digestion. Sampling continued for approximately 5 weeks or until equilibrium was reached. At this time, the first salinity change was made where half of the freshwater was replaced with seawater ($\sim$28 °/oo). Subsequent salinity changes were made to attain values of 21 °/oo and 28 °/oo in the columns.

The three smaller plexiglass columns were used to study pH effects using one sediment for each experimental series. These experiments were only operated under oxic conditions with compressed air and the same ratio 1:20 of sediment to water was employed. No salinity changes were attempted in the pH series. The three pH values used were

1. Throughout this work Millipore-type (cellulose acetate) membrane filters were used. The filters were soaked in 0.05M phthalate buffer (pH=3.6) for several hours and rinsed in deionized water before using.

the natural pH of approximately 7 and adjusted pH's of 5 and 10. The pH 5 buffer (0.1M) was an acetate buffer made by dissolving 86.59 g of sodium acetate and 25.64 ml of glacial acetic acid in 15 liters of Still Creek water. The pH 10 buffer was a carbonate buffer (0.1M) made by dissolving 87.45 g of sodium carbonate and 50.70 g of sodium bicarbonate in 15 liters of Still Creek water.

The various combinations of oxygen, pH, salinity and sediment employed in the column studies are summarized in Table VII.

During all column studies, in addition to trace metal analyses, color, turbidity and pH measurements were made periodically until no significant change was apparent. Also, water in the columns before and after each change was analyzed for color, turbidity, pH, residue, on evaporation, dissolved inorganic and dissolved organic carbon, nitrate nitrogen, chloride, sulphate, hardness, calcium, alkalinity, acidity, conductivity and salinity.

All column studies were conducted at room temperature (22-23 $^{\circ}$C).

B. Elutriate Studies

1. Sampling

(a) <u>Sediments</u>: The sediments collected on 19 April 1978 for the column experiments were used in these studies.

(b) <u>Water</u>: Laboratory tap water was used as the freshwater source allowing at least 10 minutes to

Table VII : Combination of Environmental Conditions Used in Static Column Studies

Experiment[1]	Oxygen Conditions	pH	Salinities (^{o}/oo)[2]
1	oxic [3]	natural (~7)	0, 14, 21, 28
2	anoxic [4]	natural (~7)	0, 14, 21, 28
3	oxic	5	0
4	oxic	natural (~7)	0
5	oxic	10	0

1. Each experiment was conducted only once with both the low organic (Gilmore) and high organic (Willingdon) sediments.

2. Salinities were adjusted stepwise with a period of 5 weeks allowed for equilibrium.

3. Continous dispersion of compressed air in water column.

4. Continuous purging of water column with oxygen-free nitrogen.

purge the pipes. Seawater was obtained from PEI as discussed earlier. Water was stored at 4 $^{\circ}$C but allowed to come to room temperature before the tests.

2. Test procedure

Wet sediment equivalent to 25 g dry weight was placed in 1 liter Erlenmeyer flasks containing 475 ml of water (including interstitial water). The flask contents were agitated for 30 minutes with compressed air or nitrogen. After 1 hour of settling, 200 ml of supernatant was decanted into a plastic centrifuge tube and centrifuged for 30 minutes at 3000 rpm followed by filtration through a 0.45 μm membrane filter. The filtered water samples were acidified and stored for subsequent analysis.

For tests involving anoxic conditions, a nitrogen atmosphere was maintained over the water until it was filtered and acidified.

A blank of water with no sediment was carried through the procedure to eliminate some of the errors due to sorption on to and desorption from the apparatus.

3. Environmental conditions of elutriate test

Elutriate tests were performed with compressed air (oxic) and nitrogen (anoxic conditions) on both low and high organic content sediments at salinities of 0, 1, 4, 10 and 25 $^{\circ}$/oo and at ambient pH and adjusted pH's of 5 and 10. All tests were performed at room temperature (22-23 $^{\circ}$C). For each set of conditions the test was performed on triplicate samples and the results averaged.

II. MATERIALS AND METHODS FOR EXCHANGE BETWEEN SEDIMENTS

AND BENTHIC INVERTEBRATES

A. Organisms for Exchange Experiments

Four groups of organisms were collected for the
trace metal exchange experiments. They included an estuarine
amphipod (Anisogammarus confervicolus) taken from a
laboratory culture maintained in the Institute of Oceanography,
U.B.C. The parent stock was collected from the Squamish
estuary at the head of Howe Sound. The second organism, the
opossum shrimp (Neomysis mercedis), was taken from a laboratory
population that had been collected in the main arm of the
Fraser River near Woodward Island. Oligochaetes were
collected on May 31, 1978 in the middle of contaminated Ladner
sidechannel, which is the main harbour area for Ladner,
approximately 40 km from Vancouver, B.C. They were collected
with an Ekman dredge and sieved from the sediment with a
0.038 mm bucket sieve at the collection site. Recent surveys
have indicated Tubifex tubifex and Limnodrilus hoffmeisteri
are the dominant species at this station (Hall and Yesaki,
unpublished data). Chironomids, predominantly Chironomous sp.
and Cryptochironomous sp., were collected on June 19, 1978
in a marsh side channel adjacent to the Ladner sewage lagoon.
Samples were taken with a hand scoop from the side channel
bank at low tide and sieved with a 0.038 mm bucket sieve on
site. Both the oligochaetes and the chironomids were placed
in river water in plastic buckets for transportation to the
laboratory.

B.   Sediments and Water for the Experiments

Two contaminated sediments were collected on
May 23, 1978 at the same two stations of Still Creek and
using the same methods as discussed earlier for the sediment-
water exchange. As before, Willingdon Avenue sediment was
fine and relatively high in organic matter content, and
Gilmore Avenue sediment was relatively coarse (sandy) and
lower in organic matter. A small portion of the sediment
was used for determination of total trace metals. A geo-
chemical distribution of trace metals in sediments collected
earlier (April 19, 1978) provided some information on the
form of trace metals in the sediment.

Unchlorinated freshwater from a well at UBC was
used to set up the sediment-invertebrates exchange experiments.
The amphipods required brackish water conditions. Therefore,
seawater collected from Burrard Inlet at PEI with a salinity
of approximately 28 ^{o}/oo was diluted with well water to give
a brackish water of 7 ^{o}/oo.

C.   Experimental Setup

Trace metal exchange experiments with the
amphipods, chironomids, and opossum shrimp were set up in
wide mouth 3.64 liter (128 oz.) jars while the chambers for
experiments with oligochaetes were wide mouth 0.45 liter
(16 oz.) bottles. Sediment and water were placed in the
bottles in a ratio of 1:8 . To each amphipod microcosm
chamber, 5 g wet weight of the benthic algae, _Enteromorpha_,

was added as a food substrate. The microcosm bottles were
set up in a Percevall incubator at 10 $^{\circ}$C on a 12 hour light,
12 hour dark cycle. Compressed air was bubbled into each
chamber with care taken to prevent resuspension of the
sediment. The microcosm chambers were allowed at least 24
hours to come to equilibrium before any organisms were added.

Approximately 40 - 50 opossum shrimp, 100 amphipods
and 1 g wet weight total masses of oligochaetes and
chironomids were placed in individual bottles for the
microcosms. The numbers and masses were selected in order
to provide sufficient material for trace metal analysis. At
approximately one week intervals, organisms in the two
different sediment types were collected for analysis. Since
the analyses required relatively large numbers of organisms,
it was only possible to make duplicate analyses for some of
the oligochaete microcosms. The opossum shrimp were collected
with a large bore pipette. Amphipods were hand picked with
tweezers from the algae followed by sieving the sediment
through a 0.035 mm stainless steel Tyler sieve. Both
oligochaetes and chironomids were sieved from the sediments
with the 0.035 mm sieve, transferred to a white enamel tray
and segregated from large detritus particles with tweezers.

All organisms were rinsed with distilled water,
placed in aluminum dishes and dried at 60 $^{\circ}$C to constant
weight.

III.   ANALYTICAL PROCEDURES FOR EXCHANGE AT BOTH SEDIMENT-

WATER AND SEDIMENT-INVERTEBRATE INTERFACES

A.   Geochemical Partitioning of Sediments

1.   General

All glassware and polyethylene bottles used for geochemical extractions and in general handling and storage of samples were soaked in 50 percent hydrochloric acid for several hours and then rinsed 4 - 5 times with distilled water. Glassware and polyethylene were stored in distilled water until used. All chemicals were reagent grade.

The extraction scheme used in this study was first proposed by Engler et al. (1974). Serne (1975) utilized this scheme to partition trace metals in marine sediments. The method of Engler et al. was preferred to others since it attempts to keep the sediment as close as possible to in situ conditions for the first three extractions. Drying, grinding and exposure to atmospheric oxygen are avoided. The first three extractions, namely interstitial water, exchangeable phase, and easily reducible phase, are carried out under a nitrogen atmosphere in a glove box.

Two analytical difficulties were encountered when attempts were made to use the proposed partitioning scheme. In the moderately reducible phase, the dissolved solids were too high for atomic absorption flame spectrophotometry and the chemicals used to extract this phase were grossly contaminated with zinc. Both of these difficulties were

avoided by using an alternative geochemical extraction method which employed 0.3M hydrochloric acid rather than the citrate-dithionite buffer. Malo (1977) has shown that this technique is equally selective and somewhat more effective than the citrate-dithionite extraction. This geochemical phase will be referred to as the easily acid extractable phase (EAEP).

2. Interstitial water (IW)

Well mixed sediment was transferred from the sample bottle to a centrifuge tube with a large plastic spatula in the glove box under a positive nitrogen pressure. Enough sediment was centrifuged at 3000 rpm for two hours to provide at least 150 ml of interstitial water (IW). The IW was 0.45 μm membrane filtered, acidified to pH 1 and stored in polyethylene bottles for trace metal analysis.

3. Exchangeable phase (EP)

Preweighed centrifuge tubes (250 ml) and aluminum disposable evaporating dishes were placed in the glove box containing the sample and spatula. A portion of sediment containing about 20 g of dry material was placed in the centrifuge tube and sealed with a screw cap. Another portion of the sediment containing approximately 10 g dry material was placed in the evaporating dish. Both aliquots were weighed and the sample in the aluminum dish was dried to constant weight at 103 ^{o}C to determine the moisture content. One hundred ml of deoxygenated 1.3M ammonium

acetate (pH=7) was transferred to each centrifuge tube in the glove box. The tubes were capped and shaken for 1 hour on a Burrell wrist-action shaker and then centrifuged. The supernatant was 0.45 μm membrane filtered, acidified (pH=1) and stored in polyethylene bottles for subsequent analysis. The extracts also contained interstitial water so it was necessary to correct values for the trace metal content of the IW.

4. Easily reducible phase (ERP)

The residue from the EP was washed once with 50 ml of deoxygenated distilled water, centrifuged at 3000 rpm for 1 hour and the supernatant discarded. This was done outside the glove box but under a stream of nitrogen gas. A 3-4 g sub-sample (on a dry weight basis) of the washed sediment was transferred to a preweighed centrifuge tube in the glove box. An additional sub-sample was taken for moisture determination. One hundred ml of deoxygenated 0.1M hydroxylamine-hydrochloride, adjusted to pH 2 with nitric acid, was added to the sample, shaken for 30 minutes on the Burrell shaker and then centrifuged for 1 hour. The supernatant was filtered through a 0.45 μm membrane filter and stored for analysis.

Since the residual components of sediment are not affected by atmospheric oxygen the subsequent extractions were conducted on the open laboratory bench.

5. Organic and sulphur phase (OSP)

The sediment from the ERP was washed with 50 ml of distilled, deionized water in exactly the same manner as

previously described for the ERP except it was not protected from the air. Tubes containing the washed residue were placed in a 90 - 95 ^{o}C waterbath and 30% H_2O_2 , acidified to pH 2, was added in small aliquots until no vigorous steaming was noted. Mineral ions liberated by this digestion were extracted with 100 ml of 1.0M ammonium acetate solution, adjusted to pH 2 with nitric acid, by shaking on the Burrell shaker for 1 hour followed by filtration as previously described.

6. Easily acid extractable phase (EAEP)

The residual sediment was washed, 10 ml of 3N HCl added and immediately diluted to 100 ml with distilled water. The tubes were heated with periodic shaking in a 90 - 95 ^{o}C waterbath until temperature reached 80 ^{o}C and then continued for 30 minutes. The extract was recovered by centrifugation. The residue was washed with 10 ml of distilled water and the washings combined with the acid extract which was filtered and stored for analysis.

7. Residue phase (RP)

A weighed sub-sample (approx. 0.5 g dry wt.) of the washed residue from the previous extraction was digested on a sand bath at 180 ^{o}C with 10 ml of fuming nitric acid and 10 ml of conc.[2] hydrofluoric acid in a covered Teflon

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2. Approximate strengths of the concentrated inorganic acids used in the experimental work of this thesis were: HNO_3, 90%, 21M; HCl,36.5-38%, 12M; HF, 48-51%, 29M; and $HClO_4$, 70-72%, 9M.

beaker. Upon complete evaporation, 5 ml of conc. perchloric acid was added and evaporation continued until dry again. This was followed by successive 10 ml additions of hydrofluoric acid and evaporation until the silicate minerals were digested. The residue was dissolved in dilute hydrochloric acid and made to volume in a 50 ml volumetric flask with a 5% solution of 1:1 mixture of nitric and hydrochloric conc. acids. A separate sub-sample of sediment was taken for moisture determination and a blank was carried through the digestion procedure to account for acid impurities.

8. Total trace metal analysis (Total)

Sediment sub-samples used to determine moisture content for the exchangeable phase were finely ground in an agate mortar and approximately 0.5 g portions transferred to Teflon beakers. The sediment was digested and brought to volume in the same manner as the residue phase except that the perchloric acid was diluted with 5 ml of fuming nitric acid as a safety measure.

All these geochemical extracts were analysed for Cu, Fe, Mn, Pb and Zn using the atomic absorption spectrophotometric method described later in this chapter.[3]

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3. Precision checks were made in a previous study (Bindra and Hall, 1977) standard deviation were within 10% of the average values except for some geochemical phases containing low concentrations the deviations were as high as 25 percent.

B.   Trace Metals in Water[4]

Water samples were analyzed by atomic absorption flame spectrophotometry. A complexation-solvent extraction procedure was used due to the low levels of metals in the water (McQuaker, 1976). Two problems were encountered when attempts were made to use this procedure on the elutriate samples. The solvent formed a stable emulsion with the water and the small volume of solvent that separated from the emulsion appeared to give an enhanced signal. These problems were probably caused by extraction of oils and greases from these polluted sediments. To overcome these difficulties, water samples from elutriate tests were digested with strong acid before solvent extraction.

1. Digestion of elutriate samples

The filtered samples (100 ml) were transferred to 250 ml glass beakers and 10 ml of fuming HNO_3 + 10 ml of conc. HCl were added. Samples were evaporated to reduce the contents to approximately 35 ml followed by dilution to 100 ml with deionized water. A blank was run through the above procedure to account for any trace metals in the acids.

2. Digestion of suspended solids

Suspended solids on membrane filters were transferred to 250 ml beakers and digested in fumehood after adding 2 ml of fuming HNO_3 and 1 ml of conc. $HClO_4$. Samples were taken to dryness and then solubilized with 3 ml of a 50% solution of 1:1 , HNO_3 : HCl conc. acids. A blank was also run to correct for contamination from membrane filters and acids.

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4. To check precision eight 100 ml aliquots of a water sample collected from Still Creek were analysed for Cu, Pb and Zn by solvent extraction method. Mean concentrations and percent standard deviations for the 3 metals are: 15(3.1%), Cu; 11(4.6%),Pb; 29(3.7%), Zn.

3. Preparation of reagents

The diethyldithiocarbamate (DDC) solution was prepared by dissolving 20 g of NaDDC in 380 ml of deionized water, 0.45 μm membrane filtering and extracting with several 20 ml aliquots of methyl isobutyl ketone (MIBK) until the yellowish color of the extract disappeared. This solution was prepared fresh for each batch of samples.

The biphthalate buffer was prepared by dissolving 87.4 g of potassium biphthalate in 900 ml of deionized water, followed by the addition of 12 ml of 1N HCl and diluting to 1 liter. The buffer was extracted with 25 ml of 0.01% solution of dithizone in MIBK followed by several 25 ml aliquots of MIBK until the green residual color of dithizone was completely removed.

A standard stock solution of Cu, Pb, Zn (25 mg/l) and Fe (50 mg/l) was prepared by diluting 1000 ppm Fisher AA solutions of these elements with a 10% solution of 1:1, HNO_3: HCl conc. acids.

4. Extraction procedure

The standard stock solution was diluted with acidified water (4 ml conc. HNO_3/l) to prepare standards of 1, 3, 5, 10, 20, 30, 50, 80 and 120 μg/l for Cu, Zn and Pb and twice the concentration for Fe. All standards and 100 ml portions of water samples were transferred to 250 ml beakers. Two ml of biphthalate buffer was added and the pH adjusted to 3.6 $\pm$ 0.1 with NH_4OH or HCl. The standards and samples

were transferred to 250 ml volumetric flasks to which 10 ml
of DDC solution was added, followed by mixing, and standing
for 30 minutes. Six ml of MIBK was added to each flask and
shaken for 10 minutes on a mechanical shaker (Burrell Wrist
Action). The samples were allowed to stand for 10 minutes
to separate the phases and then deionized water was added
to bring the MIBK layer into the neck of the flask. Samples
were aspirated into the spectrophotometer after standing
for 20 minutes.

C.   Trace Metals in Benthic Invertebrates and Algae

Benthic organisms and algae samples were analyzed
for trace metals by atomic absorption spectrophotometery
after dissolution as follows.

1.   Dissolution of benthic invertebrates

In trace metal analyses of organisms, error due to
gut content is generally overlooked (Flegal and Martin, 1977).
The common practice is to keep live organisms for several
hours in clean water to empty their guts. This procedure has
been questioned since organisms may still contain significant
quantities of sediment after several hours of fasting .
Further, the procedure does not prevent organisms from
reingesting their feces. Therefore, to eliminate most of
the gut error   , organisms were digested over medium heat
in 100 ml Erlenmeyer flasks by several additions of 30%
hydrogen peroxide. One ml of fuming nitric acid was added
followed by 15 ml of distilled water before the acid

completely evaporated. Undigested sediment from organisms'
guts was removed by filtration on preweighed 0.45 μm
membrane filters.

The membrane filter and the filtered sediment
were oven dried to constant weight (103 ^{o}C). The previously
determined membrane weight was subtracted to obtain gut
sediment weight. The filters and sediments were transferred
to teflon beakers and digested similarly to the residue
phase. Solubilized material was combined with the previous
organism digestate in an Erlenmeyer flask. The combined solution
was evaporated and brought to a final volume of 10 ml (for
50 - 100 mg of organisms) or 5 ml (for 25 - 50 mg of organisms).
Trace metal content of organisms was corrected for gut content
by using gut sediment weight and separately determined total
trace metal concentration in the sediments.

2. Dissolution of benthic algae

Algal samples were cleaned with tap water and
distilled water then oven dried (70 ^{o}C). The dry material
was ground and weighed portions digested in 50% H_2O_2 followed
by fuming nitric acid. Samples were filtered to remove any
residual sediment and the filtrate diluted to 25 ml for
trace metal analysis.

D. Atomic Absorption Spectrophotometry

A Jarrell - Ash Model 810 double channel atomic
absorption spectrophotometer was used to determine Cu, Fe,
Mn, Pb and Zn in the sediment extracts, MIBK extracts of

water samples, and in the digested benthic organisms and algae. Calibration curves were prepared with diluted Fisher Standard AA Solutions. Background corrections could be conveniently made by using both channels and subtraction made by the instrument. The analytical settings for each element are summarized in Table VIII.

E. Other Analytical Techniques

1. Color

True color in water was measured with the Fisher Scientific Hellige Aqua Tester on filtered samples. Highly colored samples were diluted to within the range of the instrument (0 - 100 mg/l Pt.).

2. Turbidity

Turbidity measurements were made on vigorously agitated water samples with a Hach Turbidimeter (Model 2100A). The instrument was calibrated with Nephlene standards provided with the instrument. Results are expressed in NTU (Nephlometric Turbidity Units) or as equivalent JTU (Jackson Turbidity Units).

3. pH

A Fisher Scientific pH meter (Model 320) standardized with buffers of pH 4, 7 and 10 was used to measure pH.

4. Residue

Appropriate volumes of filtered and unfiltered

Table VIII :   Analytical Settings for Atomic Absorption
                Spectrophotometry[1]

Element	Absorbing Wavelength ($\mathring{A}$)	Temp. Current (μa)	Slit Width	Flame Stoichiometry
Cu	3247	7	5	Very slightly reducing
Fe	2483	8	3	Lean
Mn	2795	10	4	Very slightly reducing
Pb	2833/2170[2]	5	4	Slightly reducing
Zn	2138	7.5	3	Lean

1.   used air/acetylene as oxidant/fuel mixture.

2.   2833 $\mathring{A}$ for samples high in dissolved solids.

water were dried overnight at 103 °C in preweighed aluminum dishes. On cooling in a dessicator, dishes were reweighed to determine total and dissolved solids.

5. Dissolved carbon

Total carbon and inorganic carbon were measured on filtered samples with a Beckman Total Carbon Analyzer (Model 915). Organic carbon was determined by difference. Samples containing high levels of inorganic carbon relative to organic carbon were acidified with HCl and purged before measuring the organic carbon on the total carbon channel.

6. Hardness, calcium, alkalinity and acidity

These water quality parameters were measured by standard techniques outlined in Standard Methods (APHA, AWWA and WPCF, 1975). The EDTA titrimetric method was used for hardness and calcium measurements. Acidity samples were titrated with 0.1N NaOH to pH 8.3 .

7. Nitrate, chloride and sulphate

These anions were also quantitated by Standard Methods techniques (APHA, AWWA and WPCF, 1975). Nitrate nitrogen was measured by the UV absorption techniques using a Pye Unicam SP8-100UV spectrophotometer. Chloride was titrated using the mercuric nitrate method and sulphate was determined by turbidimetry.

8. Conductivity and salinity

A Radiometer Conductivity Meter (Model COM3)

was used to measure conductivities of water samples. Water samples and 0.0100N KCl solution were allowed to come to room temperature and then temperature and specific conductivity were measured. Knowing the specific conductance of 0.0100N KCl as a function of temperature allowed sample conductivities to be corrected to 25 $^{\circ}$C. Salinity was determined from chloride measurement by the following relationship.

$$\text{Salinity } (^{\circ}/oo) = (1.80655) \cdot (Cl^- \text{ g/l})$$

9. Weight loss on ignition

Weighed sediment samples dried at 103 $^{\circ}$C were placed in preweighed crucibles and combusted in a muffle furnace at 600 $^{\circ}$C for 3 hours. Weight loss represented the organic matter content of the sediment.

10. Particle size analysis

Sediment samples were dried at 150 $^{\circ}$C and disaggregated in a large mortar. Fifty to one hundred grams of disaggregated sediment were separated by shaking for 4 minutes on a nest of Standard Sieves made up of No. 18, 35, 60 and 230 which have mesh sizes of 1, 0.5, 0.25 and 0.063 mm respectively. The five size fractions were labelled from coarse to fine as (a) very coarse sand, (b) coarse sand, (c) medium sand, (d) fine and very fine sand, (e) silt and clay.

Chapter 3

RESULTS

I.   TRACE METAL EXCHANGE BETWEEN SEDIMENTS AND WATER

A.   Characteristics of the Sediments

1.   Sediment trace metal geochemistry

The geochemical distribution of the trace metals,

Cu, Fe, Mn, Pb and Zn in the sediments used in the column and

elutriate sediment-water exchange studies is presented in

Tables IX and X.   The sediment described in Table IX was

collected on Dec. 23, 1977 and used in the oxic[1], anoxic,

salinity, and low organic - pH column studies.   The sediment

described in Table X was collected on April 19, 1978 and was

used for the high organic - pH column studies and the

elutriate tests.   During the period between collection of the

two sediment samples there was an increase in the total trace

metal levels in sediments from both stations.   The Willingdon

station showed the greatest increase with the concentrations

of total Cu, Pb and Zn increasing by factors of approximately

5, 7 and 2.5 respectively.   Sediment contamination during

this period resulted in a large increase in most trace metals

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1.   Terms 'oxic' and 'anoxic', when used to express experi-
     mental conditions of sediment-water exchange studies of
     this thesis, signify: oxic-continuous dispersion of
     compressed air, anoxic-continuous purging with oxygen-
     free nitrogen (see chapter 2).

Table IX :   Trace Metal Distribution in Sediments from the Brunette Basin Used in
Sediment-Water Exchange Studies (December 23, 1977)[1].

Trace Metal	Station	Sediment Geochemical Fraction							
		IW	EP	ERP	OSP	EAEP	Residue	Sum	Total
Copper	Gilmore	0.02	0.08	2.98	47.0	9.52	9.08	68.7	66.1
	Willingdon	0.13	0.11	2.82	57.8	19.4	7.05	87.8	71.4
Iron	Gilmore	0.16	1.90	592	133	3460	15200	19400	19400
	Willingdon	2.21	3.81	777	1180	9280	20600	31800	31400
Lead	Gilmore	0.04	3.81	35.2	62.1	35.0	37.8	174	171
	Willingdon	0.12	1.08	5.89	80.0	25.3	25.0	137	138
Manganese	Gilmore	0.58	31.1	41.9	6.74	34.3	432	547	441
	Willingdon	6.90	18.4	30.6	24.6	89.6	443	613	560
Zinc	Gilmore	0.38	1.61	23.2	27.4	21.8	34.8	109	101
	Willingdon	0.35	1.42	27.0	62.7	26.8	33.1	151	181

1. All values are in ppm (μg/g) on oven dry (103°C) basis. Sediment used in oxic, anoxic,
    salinity and low organic-pH column studies.

2. IW = interstitial water, EP = exchangeable phase, ERP = easily reducible phase ,
    OSP = organic and sulphur bound phase , EAEP = easily acid extractable phase.
    Total determined independently.

Weight loss on ignition : Gilmore = 2.4%, Willingdon = 9.97%

Table X :   Trace Metal Distribution in Sediments from the Brunette Basin Used in
Sediment-Water Exchange Studies (April 19,1978)[1].

Trace Metal	Station	Sediment Geochemical Fraction[2]							
		IW	EP	ERP	OSP	EAEP	Residue	Sum	Total
Copper	Gilmore	0.01	0.13	17.2	67.8	11.4	11.8	108	125
	Willingdon	0.06	0.13	28.9	208	32.8	12.8	283	328
Iron	Gilmore	0.22	232	1520	443	3270	15700	21200	22600
	Willingdon	42.6	66.6	2180	789	4870	19300	27200	26100
Lead	Gilmore	0.04	4.8	120	56.4	24.7	26.2	232	253
	Willingdon	0.09	32.3	555	304	96.3	44.5	1032	980
Manganese	Gilmore	1.35	55.6	44.3	10.6	35.5	353	502	549
	Willingdon	7.05	60.8	56.1	17.7	45.7	398	586	525
Zinc	Gilmore	0.16	5.8	61.5	36.6	17.9	38.0	161	162
	Willingdon	0.35	30.0	216	110	34.9	26.8	418	450

1. All values are in ppm (μg/g) on oven dry (103°C) basis. Sediment used for high organic-pH
    column and elutriate studies.

2. IW = interstitial water, EP = exchangeable phase, ERP = easily reducible phase, OSP = organic
    and sulphur bound phase, EAEP = easily acid extractable phase. Total determined independently.

Weight loss on ignition : Gilmore = 2.6% , Willingdon = 6.76%

in the exchangeable and easily reducible phases. There was
also a 30% decrease (9.97 - 6.67% change) in the organic
content of the Willingdon sediment.

2. Sediment particle size distribution

Particle size distribution of sediments obtained
from Willingdon Avenue and Gilmore Avenue stations in the
Still Creek area of the Brunette Basin is presented in
Table XI. This particle size analysis is from a field survey
of sediments carried out earlier in four different areas of the
Lower Mainland of British Columbia(Bindra and Hall,1977). The
analyses indicate that high organic Willingdon sediment is
fine and consists of fine to very fine sand (53%) and silt
and clay (38.2%). In contrast, Gilmore low organic sediment
is mostly (>87%) medium to coarse sand.

B. Dissolved Trace Metal Exchange in Static Columns
at Different Oxygen and Salinity Conditions

The concentrations of dissolved trace metals, Cu,
Fe, Pb and Zn in the columns containing the two sediments and
subjected to different oxygen and salinity conditions are
presented in Figures 4, 5, 6 and 7.

1. Copper (Cu)

The initial concentrations of dissolved Cu very
rapidly dropped to values of less than 10 μg/l for both
sediments under both oxic and anoxic conditions (Figure 4).
Dissolved Cu in the low organic sediment columns reached an

Table XI :   Particle Size Distribution of Sediments at Two
Stations on Still Creek (Brunette Basin) Sampled
for Trace Metal Exchange Studies (Bindra and Hall,
1977)

Station No.	Description	Particle Size Analysis (%)				
		1	2	3	4	5
11	Still Creek at Willingdon Ave.	0.2	1.2	7.4	53.0	38.2
12	Still Creek at Gilmore Ave.	2.0	33.5	53.7	8.0	2.9

1 = very coarse sand (2-1 mm), 2 = coarse sand (1-0.5 mm),

3 = medium size sand (0.5-0.25 mm), 4 = fine and very fine

sand (0.25-0.063 mm), 5 = silt and clay ($<$0.063 mm).

Figure 4.   Dissolved Copper in Microcosms Under Oxic and Anoxic Conditions
at Different Salinities.
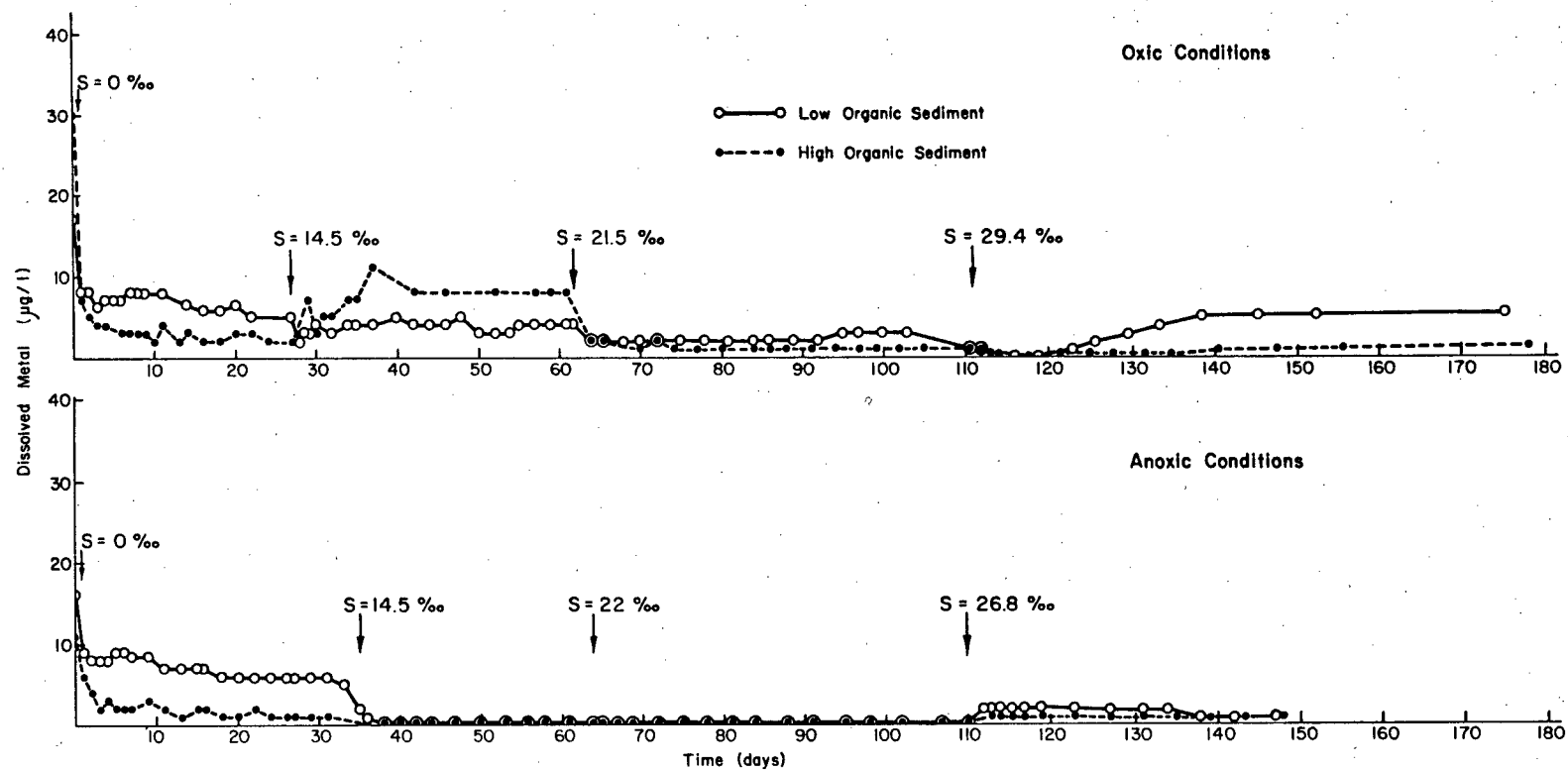
equilibrium concentration which was twice as high as values for the high organic sediment even though the high organic sediment contained a slightly higher total Cu concentration. After the first salinity change, the dissolved Cu in the anoxic column dropped to less than the detection level and remained low throughout subsequent salinity increases. In the aerobic system (Figure 4), dissolved Cu increased to approximately 10 μg/l in the high organic sediment during the first salinity increase (14.5 ^{o}/oo) but decreased to 1-2 μg/l upon subsequent salinity changes. In the low organic oxic column the dissolved Cu did not increase to as high of concentration as in the high organic column during initial salinity additions but during the final salinity change it established a higher equilibrium concentration of 5 μg/l.

2. Iron (Fe)

Dissolved Fe in the oxic system (Figure 5) reached an equilibrium concentration of approximately 70 μg/l after 15 days. Salinity adjustments in the oxic columns caused dissolved Fe concentrations to fall to less than 10 μg/l for both high and low organic sediments. Under anoxic conditions (Figure 5) the column containing the low organic sediment with the lower total Fe level (19,400 ppm) released Fe into solution reaching values over 2 mg/l. After the first and second salinity adjustments there was an initial drop in dissolved Fe levels followed by a large release of Fe

Figure 5. Dissolved Iron in Microcosms Under Oxic and Anoxic Conditions at Different Salinities.
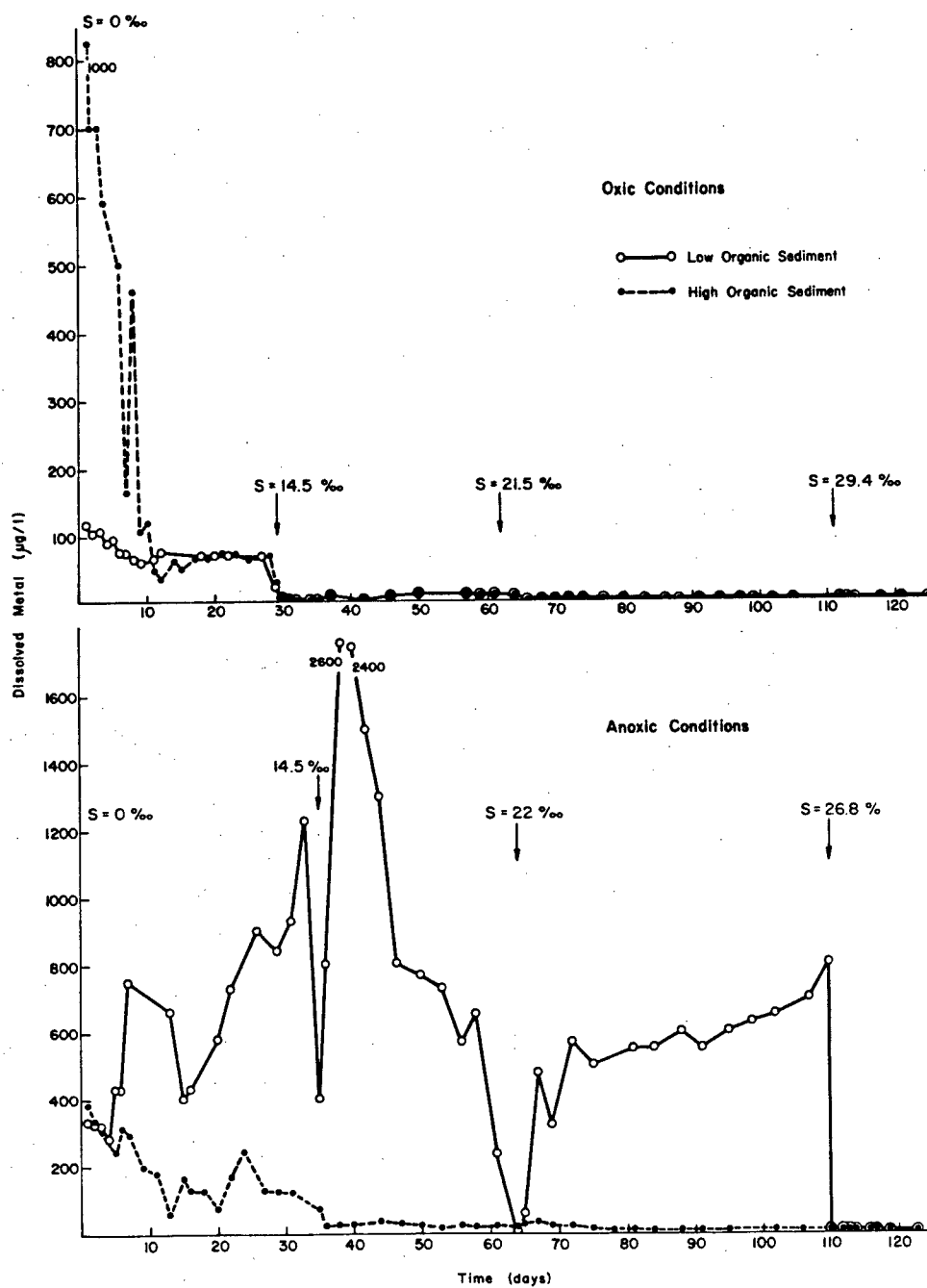
into solution. When the salinity was adjusted to full seawater, Fe values dropped to the detection level of 1 μg/l in this column. In the high organic sediment system with higher sediment Fe levels (31,400 ppm), the dissolved Fe levels dropped to the detection level after the first salinity adjustment and remained low.

3. Lead (Pb)

In the oxic columns, dissolved Pb in both the high and low organic sediment systems showed a similar pattern (Figure 6). During the initial equilibrium stage with freshwater there was an equilibrium level between 5 and 10 μg/l Pb. The first salinity change removed the metal from solution but there was some release after 5 days from both sediments which stabilized at 7 μg/l. Dissolved Pb was removed in the oxic systems after the second salinity adjustment. In the anoxic system there was a gradual decrease in dissolved Pb in freshwater (Figure 6). Lead decreased to the detection level after the first salinity adjustment in the anoxic system.

4. Zinc (Zn)

Under oxic conditions (Figure 7) there was an initial removal of dissolved Zn reaching an equilibrium concentration between 3 and 5 μg/l after 12 days. The first salinity increase caused release of Zn into solution with the low organic sediment system reaching an equilibrium concentration of approximately 25 μg/l. The second salinity

Figure 6. Dissolved Lead in Microcosms Under Oxic and Anoxic Conditions
at Different Salinities.
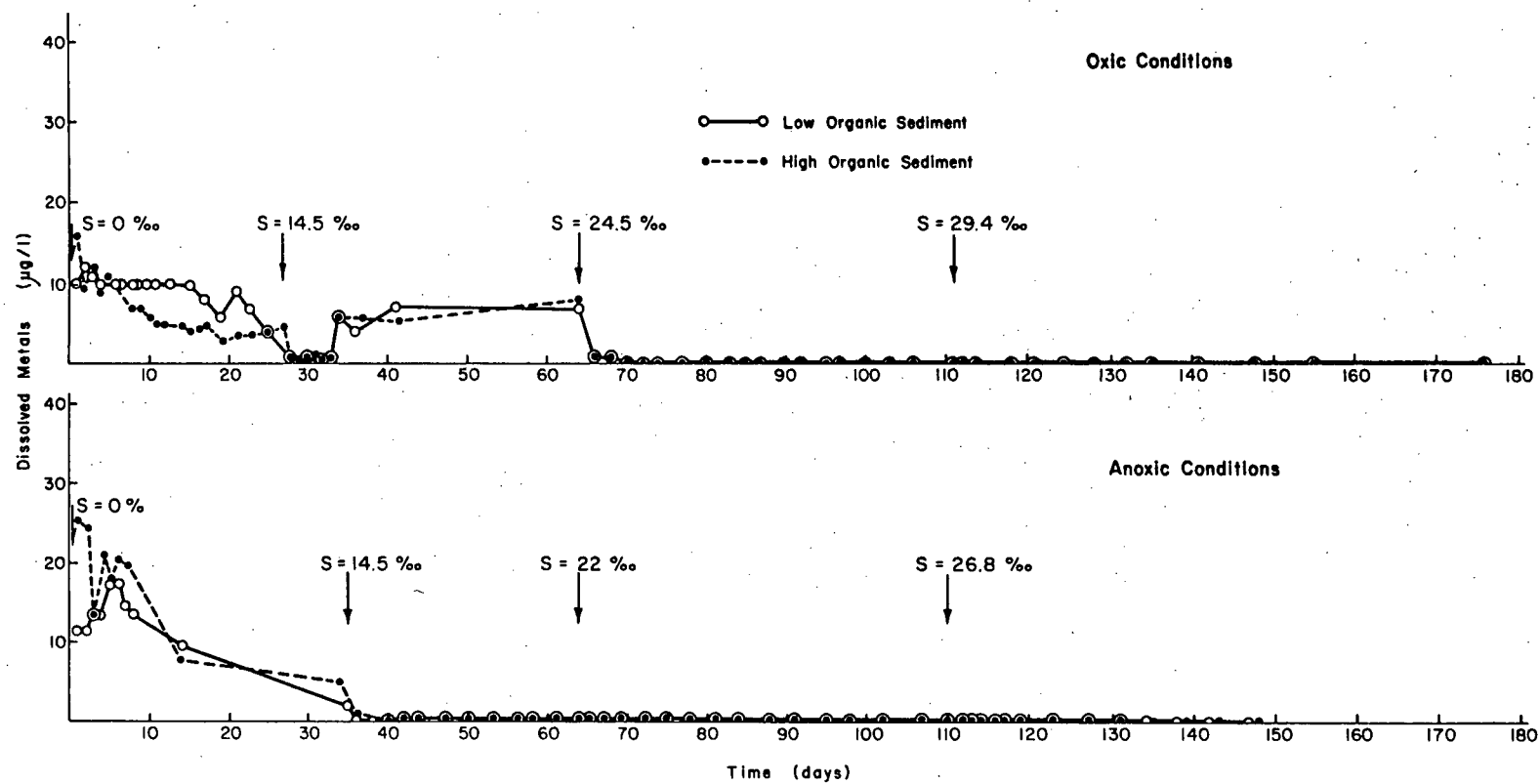
Figure 7. Dissolved Zinc in Microcosms Under Oxic and Anoxic Conditions at Different Salinities.
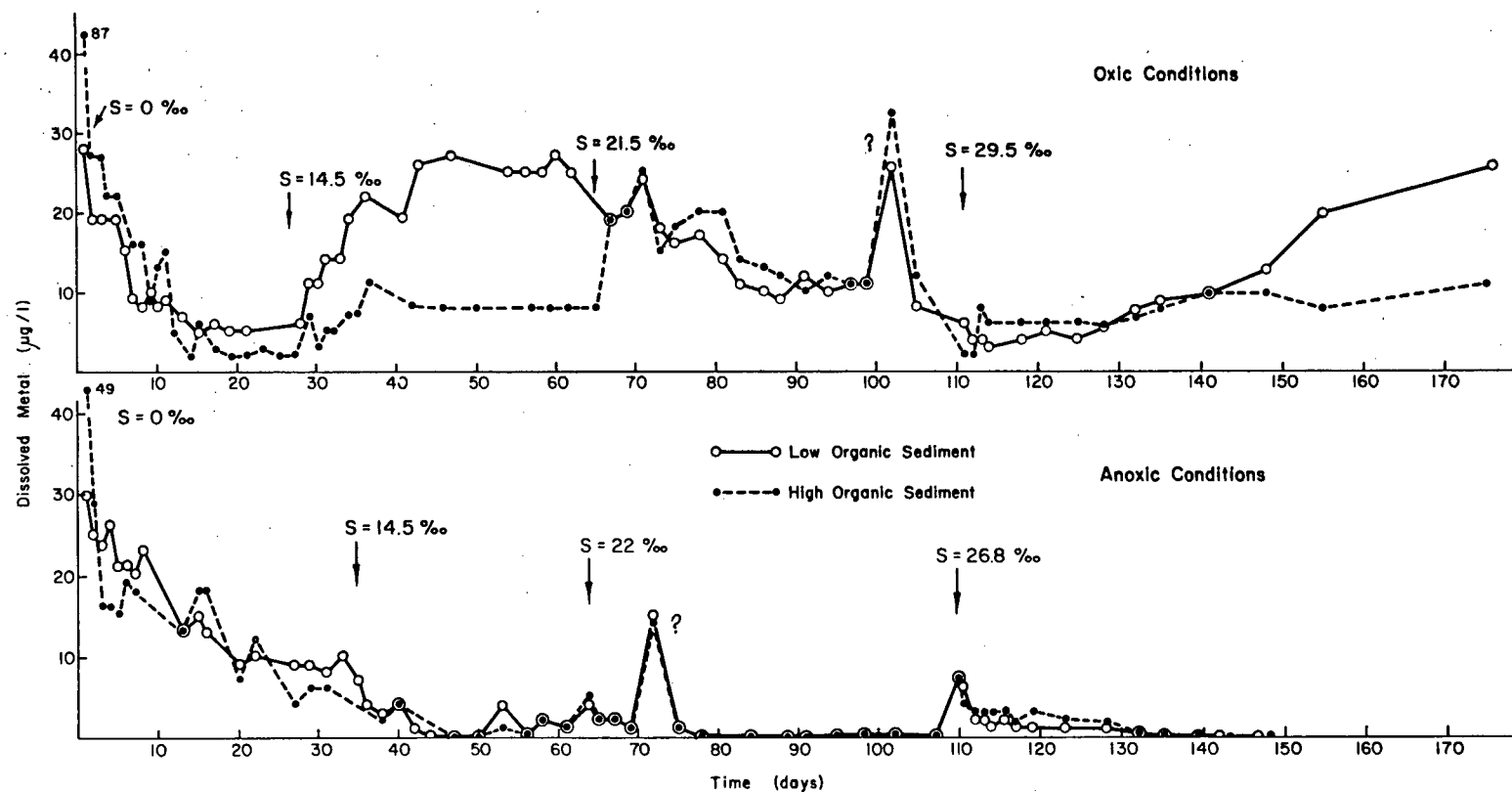
change initiated a slow removal of Zn from solution with one sporadic increase attributable to analytical contamination. After the final salinity change, there was a gradual release of Zn from both sediments which was still occurring after two months. In the anoxic system (Figure 7), Zn was gradually removed from solution over the 30 day freshwater period. After the first salinity change, Zn was rapidly removed from solution and remained low throughout subsequent salinity changes with some sporadic increases attributed to resuspension of particles or analytical error.

5. Water quality conditions in sediment microcosms

The water quality conditions in the columns subjected to different oxygen conditions and a series of salinity changes are presented in Appendix A (Tables A1 to A4). Both initial and final water quality conditions are presented for each salinity change. After the first seawater addition, the system was dominated by the quality of the seawater which buffers any minor changes that take place due to the exchange reactions with the sediment. There was a general increase in the pH of all columns between each salinity change which could be attributable to purging of carbon dioxide from the water. Alkalinity values showed a general decrease between each incremental salinity change. However, under anoxic conditions in freshwater, there was an increase in alkalinity probably reflecting dissolution of carbonates under the low redox conditions. An increase in dissolved

solids (30 - 45 mg/l) in the oxic systems occurred for both sediments during the freshwater incubation period. This increase could not be accounted for by the water quality parameters measured. Changes in dissolved solids in the anoxic systems under freshwater conditions were smaller and showed no consistent pattern.

C. Effect of pH on Dissolved Trace Metal Exchange

The effect of three pH's (5, 7 and 10) on the exchange of dissolved Cu, Fe, Pb and Zn in oxic columns containing both high and low organic sediments is presented in Figures 8, 9, 10 and 11.

1. Copper (Cu)

Dissolved Cu concentrations were much higher at low and high pH's than at the ambient pH of 7 (Figure 8). In the low organic sediment equilibrium concentrations of 40 and 80 μg/l occurred in the pH 5 and 10 systems respectively. For the high organic sediment at low pH there was a rapid release of Cu with a gradual removal over a month period. At high pH there was gradual release of Cu from this sediment over the entire study period. Final concentrations of Cu in the high organic sediments were approximately twice the level for the low organic sediments in the pH 5 and 10 systems.

2. Iron (Fe)

Dissolved Fe concentrations were higher in the

Figure 8.   Effect of pH on Dissolved Copper Exchange in
Microcosms (Oxic Conditions, Salinity<1 °/oo).
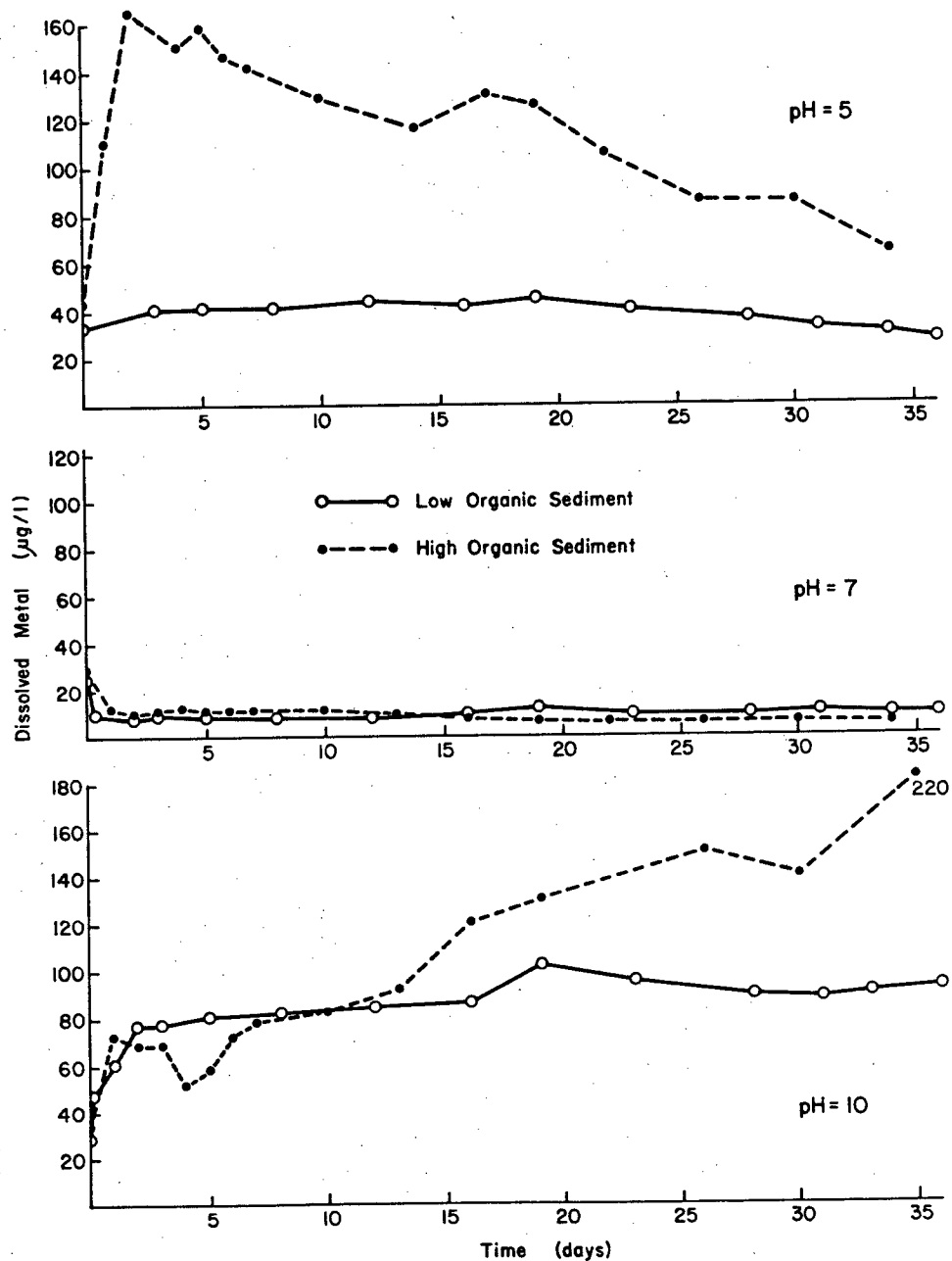
Figure 9. Effect of pH on Dissolved Iron Exchange in Microcosms (Oxic Conditions, Salinity <1 °/oo).
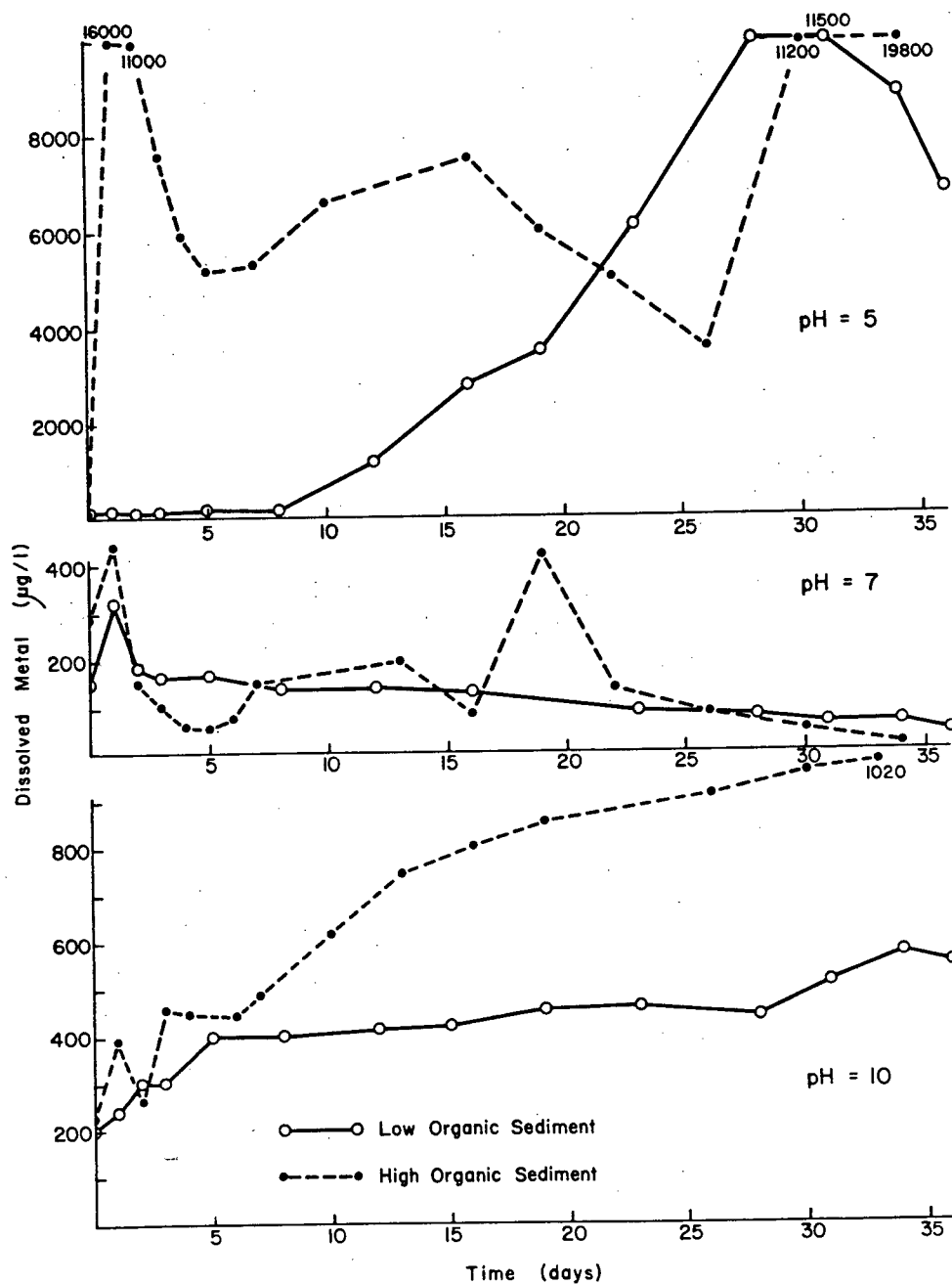
Figure 10. Effect of pH on Dissolved Lead Exchange in Microcosms (Oxic Conditions, Salinity <1 $^\circ$/oo).
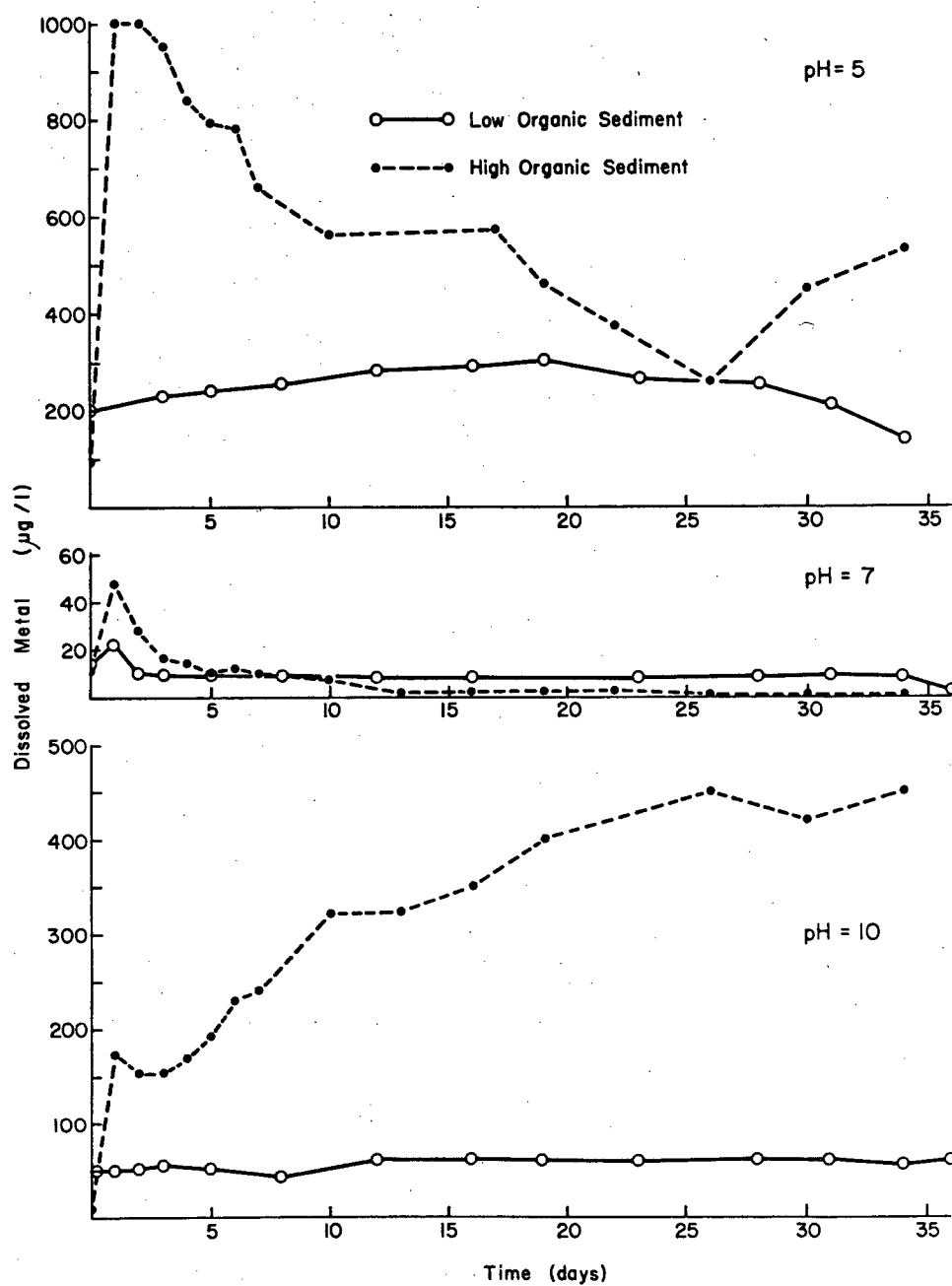
Figure 11. Effect of pH on Dissolved Zinc Exchange in Microcosms (Oxic Conditions, Salinity 1<°/oo).
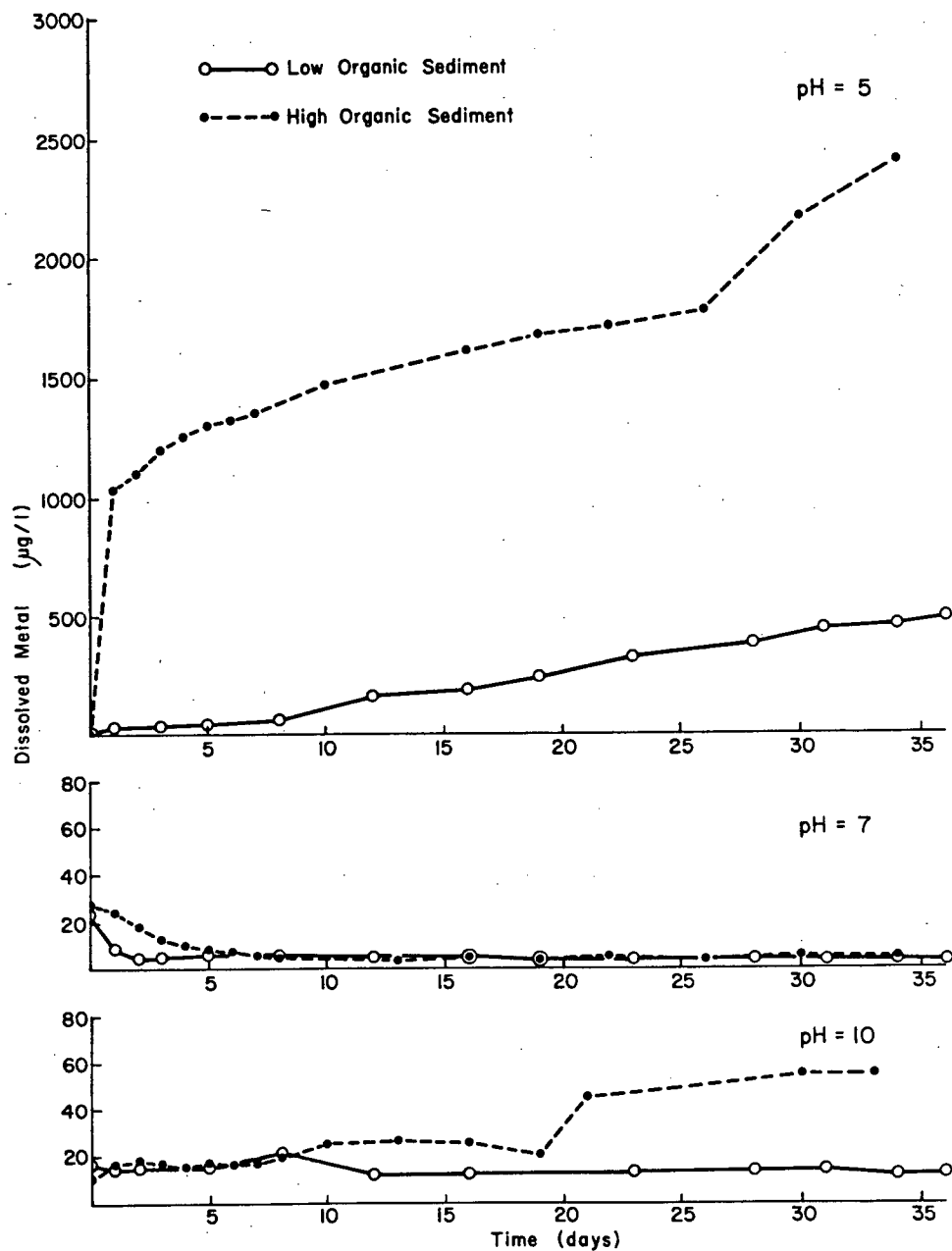
low and high pH systems when compared to the ambient (pH 7)
system except during the initial incubation period (Figure 9).
The release of Fe in the high pH system was very similar to that
of Cu with the high organic sediment system reaching twice the
concentration level found in the low organic sediment. In
the pH 5 system (Figure 9) there was a rapid release of Fe
from the high organic sediment followed by a gradual decrease
and final increase when the gradually rising pH was adjusted
back to 5. The low organic, low pH system did not release
Fe until after one week then concentrations increased to levels
found in the high organic system (11.5 mg/l).

3. Lead (Pb)

Release of Pb from the sediments showed a response
similar to Cu. The high and low pH systems showed a greater
release of Pb than the ambient pH 7 system (Figure 10). The
low organic sediment system achieved a rapid equilibrium with
the values of 50 and 200 μg/l for the pH 10 and 5 treatments.
For the high organic sediment at pH 10 there was a gradual
release of Pb over the month incubation period.

4. Zinc (Zn)

Similar to the other trace metals, there was
greater release from the high and low pH than at ambient pH
with a greater release from the high organic sediment
(Figure 11).

5. Water quality conditions in the variable pH sediment systems

The thirteen water quality parameters measured in each pH system for the two different sediments are summarized in Appendix A (Tables A5 and A6). The water quality measurements were made at the beginning and end of the experiment. In the pH 5 system the total organic carbon content, acidity, and alkalinity were high due to the acetate used to buffer the pH at 5. In the high pH system the inorganic carbon and alkalinity values were high due to bicarbonate-carbonate buffer used to keep the pH at 10. This high pH resulted in dissolution of organic matter from the sediment as indicated by the great increase in true color and total organic carbon. These organic compounds are probably 'humic-like' substances since they are very colored and dissolve at high pH. In the low pH systems a gradual pH increase was taking place but during the first experiment with low organic sediment the increase was delayed and slower. The increase was probably attributable to microbial breakdown of the acetate buffer and the delay and slower action for the first run was due to lag in development of a sufficient active population of acetate consuming bacteria. After 27 days, the second, low pH high organic sediment system was adjusted back to initial pH level of 5. The high nitrate concentration was most likely due to interference of color in the ultraviolet absorption technique used to

measure this ion.

D. Effect of pH on Particulate and Dissolved Trace Metal Exchange

In addition to monitoring the dissolved trace metals in the pH microcosms, samples were periodically analyzed for particulate trace metals. The dissolved and particulate trace metals in the columns at pH 5, 7 and 10 containing high and low organic matter are presented in Appendix B (Tables B1, B2 and B3). The results for the pH 5 column are also presented in Figure 12 to show the effect of upward drifting pH on the turbidity and particulate and dissolved trace metal exchange. The pH 7 and 10 columns had no significant drift in pH over the duration of these experiments.

1. pH 5

In the low organic column, pH gradually increased from 4.93 → 5.50 (Figure 12). Turbidity dropped quickly after the first day and began to increase slowly after day 26 when pH increased beyond 5.10 . Beyond pH 5.10 the dissolved Cu and Pb began to come out of solution. Iron came out of solution above pH 5.3 whereas Zn was still dissolving at the final pH of 5.5 .

Particulate Cu, Fe, Pb and Zn were high at the beginning of the experiment, coincident with high turbidity (Figure 12). Particulate associated metals dropped to low

Figure 12. Dissolved and Suspended Particulate Trace Metals in a Microcosm at pH 5 (Oxic, S <1 °/oo).

HIGH ORGANIC SEDIMENT   LOW ORGANIC SEDIMENT
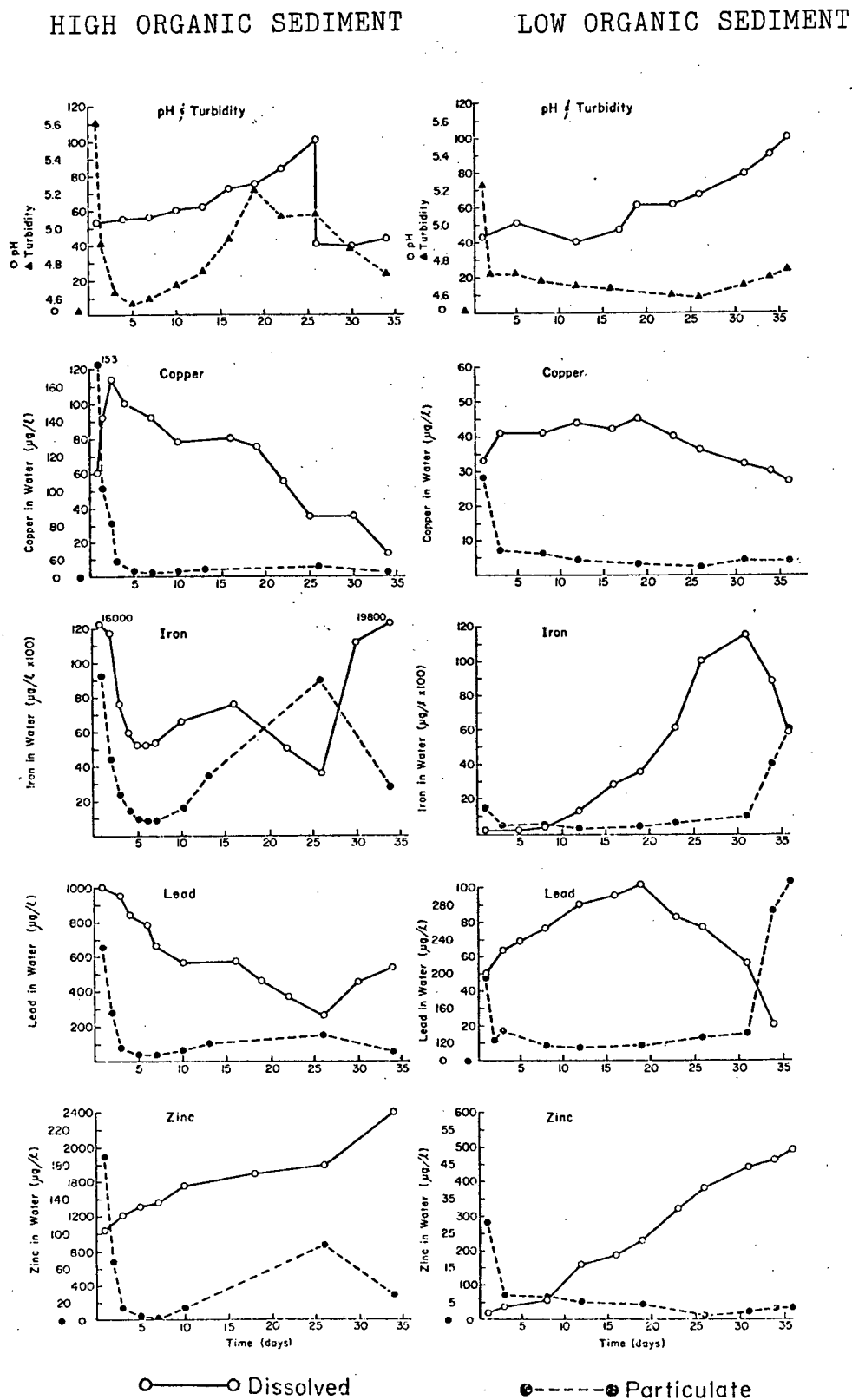
values at the second day and remained low except particulate
Fe and Pb which increased after 30 days when pH went above
5.3 , again coincident with a slight increase in turbidity.

In the high organic columns at pH 5, there was a
much faster increase in pH which was readjusted to pH 4.9
after 26 days (Figure 12). With the exception of Zn, the
dissolved trace metals gradually decreased until the pH was
readjusted which released more Fe and Pb into solution.
Dissolved Zn increased continually over the test period , as
was the case with low organic sediments.

Particulate Fe, Pb and Zn followed turbidity very
closely with high initial values that dropped very rapidly,
then slowly increased as pH increased and dropped when the
pH was readjusted back to 4.9 .

2. pH 7

In both sediments, there was an initial release of
dissolved metals and particulate associated metals were
high (Table B2). Both dissolved and particulate metals
gradually decreased throughout the equilibration period.

3. pH 10

In both columns (Table B3) there was an initial
suspension of particulate associated trace metals which
gradually decreased as the columns came to equilibrium. In
the high organic system the concentrations of dissolved
metals increased towards the end of the experiment whereas
in the low organic columns, dissolved metals reached an

equilibrium concentration after approximately a week to 10 days. However, during the fifth week, dissolved Fe concentrations showed some increase in the low organic system.

4. Comparison of different pH columns

The final concentrations of dissolved and particulate associated trace metals at the different pH's after 34 days of equilibration are summarized in Figure 13. It is quite evident that both the low and high pH cause a greater release of trace metals from sediment than occurs at neutral pH. There are usually higher trace metal concentrations in the dissolved phase at these high and low pH's. With the exception of Fe, there was a much greater release of trace metals from the high organic sediment which had a higher total trace metal concentration and higher levels in the exchangeable and easily reducible geochemical phases.

E. Dissolved Trace Metal Exchange in Agitated Water-Sediment Systems (Elutriate Test)

1. Effects of oxygen and salinity

The release and uptake of dissolved Cu, Fe, Pb, Mn and Zn in agitated systems under different oxygen (oxic and anoxic, see footnote P.89) and salinity conditions are summarized in Figure 14. Both the high and low organic sediments were equilibrated under all conditions. A greater number of lower salinity values were used in the elutriate procedure since the column studies indicated that the interesting exchanges were taking place between 0 - 10 ^{o}/oo salinity. The negative

Figure 13. Final Concentrations of Dissolved and Particulate Trace Metals in Microcosms at Three Different pH's (Oxic, S< 1 ^{o}/oo).
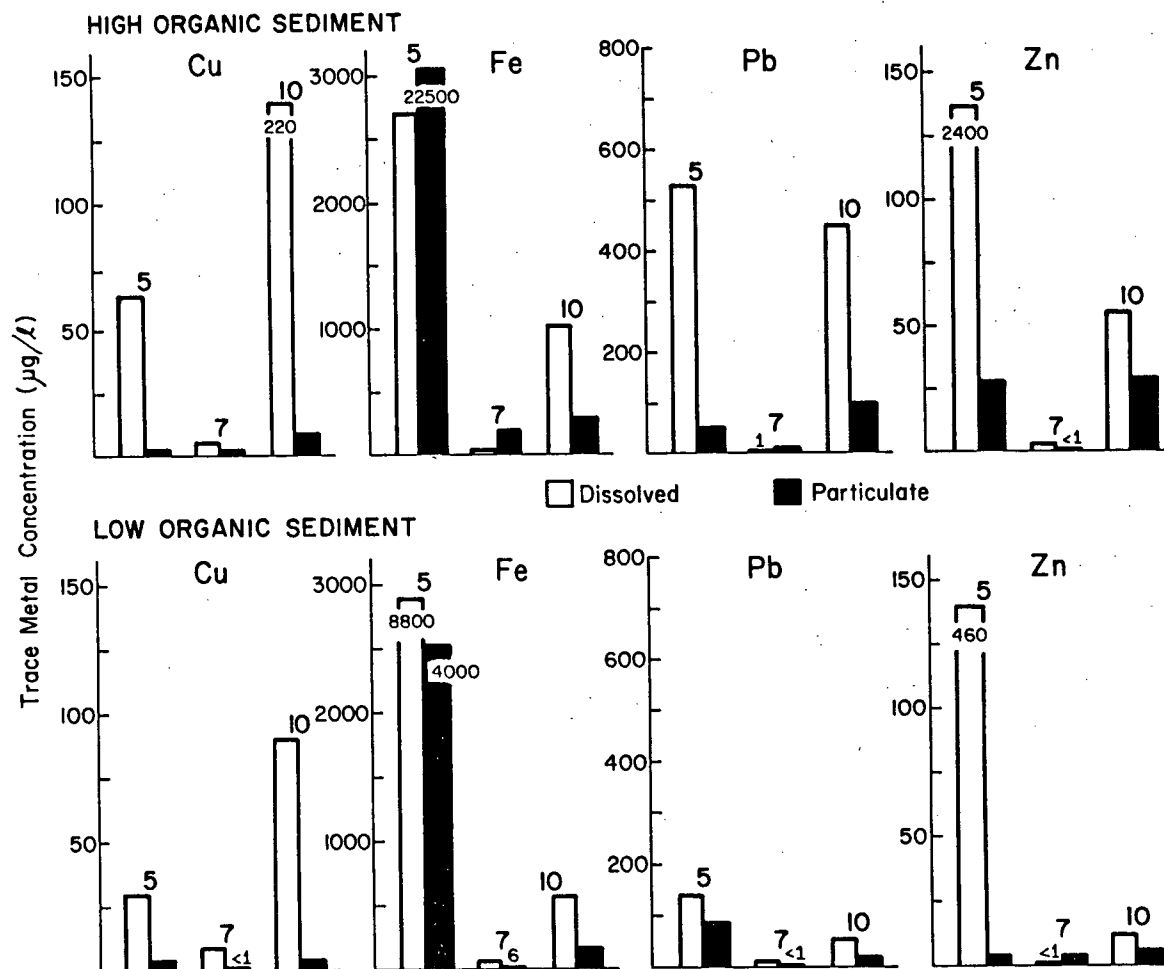
Figure 14. Exchange of Dissolved Trace Metals in the Elutriate Test Under Oxic and Anoxic Conditions and Different Salinities.

●- - - -● high organic   O——————O low organic
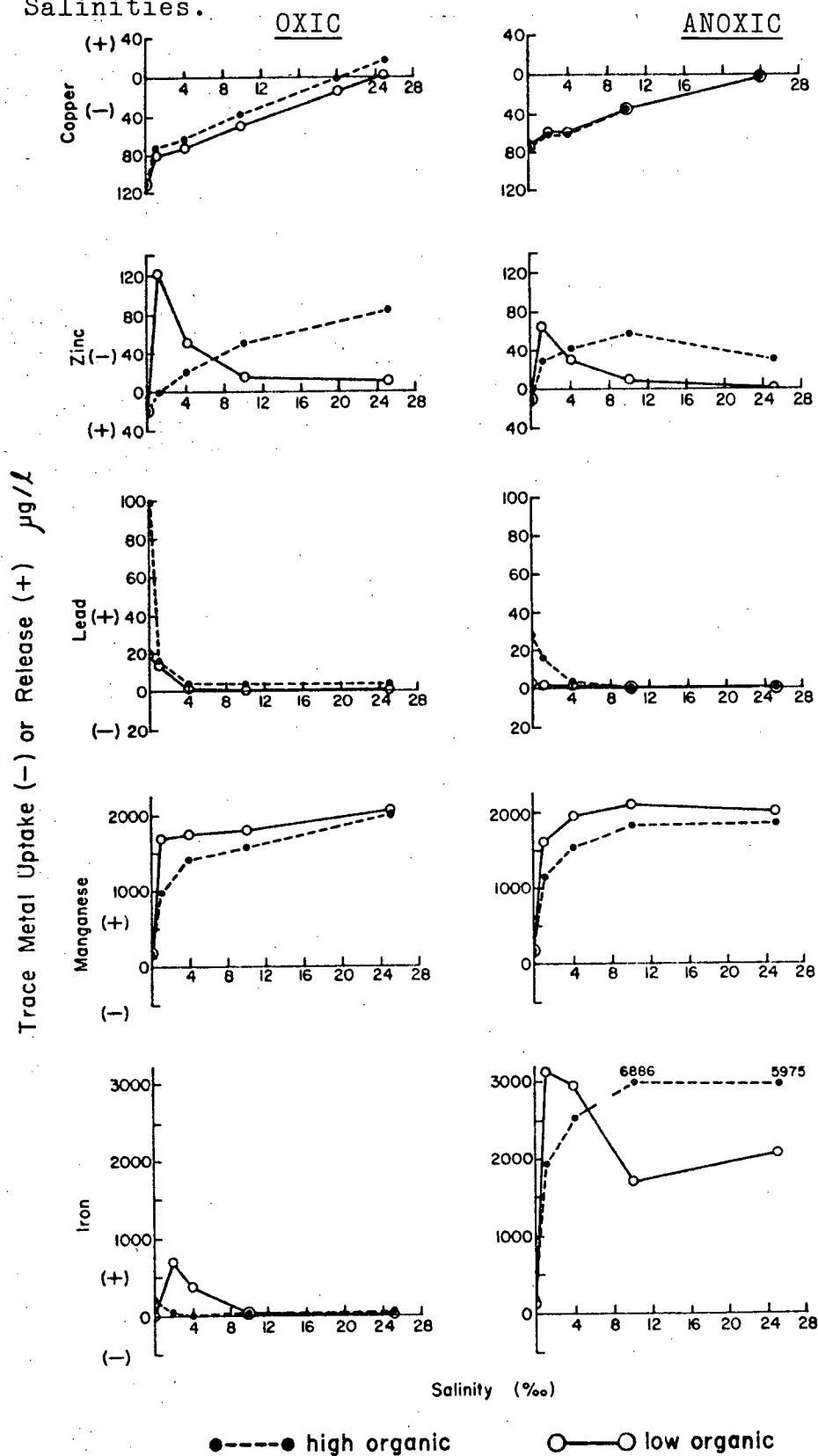
(-) values on Figure 14 refer to uptake of dissolved element by the sediment while positive (+) values indicate release from the sediment.

Copper was removed from solution by both the high and low organic sediments under both oxic and anoxic conditions. The amount of Cu taken up by the sediment decreased as the salinity increased because the seawater had a lower Cu concentration and effectively diluted the Cu in the freshwater. However, expressed on a percent removal basis the effect of changing salinity on Cu removal was negligible.

Under oxic conditions there was some release of Fe by the low organic sediment at low salinities (0-4 ^{o}/oo) whereas there was no Fe exchange from the high organic sediment. Under anoxic conditions Fe was released from both the high and low organic sediments over a wide salinity range. For the low organic sediment maximum release occurred at low salinities.

Lead was released from the high organic sediment in freshwater under both oxic and anoxic conditions. Increases in salinity caused a rapid removal of Pb from solution with values decreasing to the detection level at 4 ^{o}/oo salinity for both sediments under high and low redox conditions.

There was a release of Mn by both sediments under oxic and anoxic conditions. Release increased with increasing salinity reaching a plateau at 4 ^{o}/oo salinity with a Mn concentration between 1500 - 2000 μg/l.

Concentration levels were slightly higher for the low organic sediment even though the total Mn and geochemical distribution in the two sediments was similar.

Zinc was taken out of solution in freshwater for both sediments under oxic and anoxic conditions. A slight increase in salinity (1 $^o/oo$) caused Zn to be released by the low organic sediment. As salinity increased in the low organic sediment system, Zn was removed from solution. In the high organic sediment there was a gradual increase in the release of Zn as salinity increased both under oxic and anoxic conditions.

2. Effect of pH

The effects of pH on the exchange of trace metals in sediments using the elutriate test are summarized in Figure 15. In general there was a greater release of trace metals at pH 5 and pH 10 than at the natural pH of 7. The elutriate test results compared favorably with the observations made with the static columns.

For Fe, Mn and Pb, metal was released into solution for both the high and low organic sediments at all three pH's. The greatest release occurred at pH 5 for three metals. There was no consistent trend for release of Fe, Mn and Pb from the high or low organic sediments in spite of the greater concentration of most metals in the high organic sediment.

Both Cu and Zn were adsorbed to the sediments at

Figure 15. Exchange of Dissolved Trace Metals in the Elutriate Test at Different pH's (Oxic Conditions, Salinity < 1 $^o/_{oo}$).

Values along the vertical axes are in μg/l

☐ High Organic Sediment

■ Low Organic Sediment

Numbers above histogram indicate pH
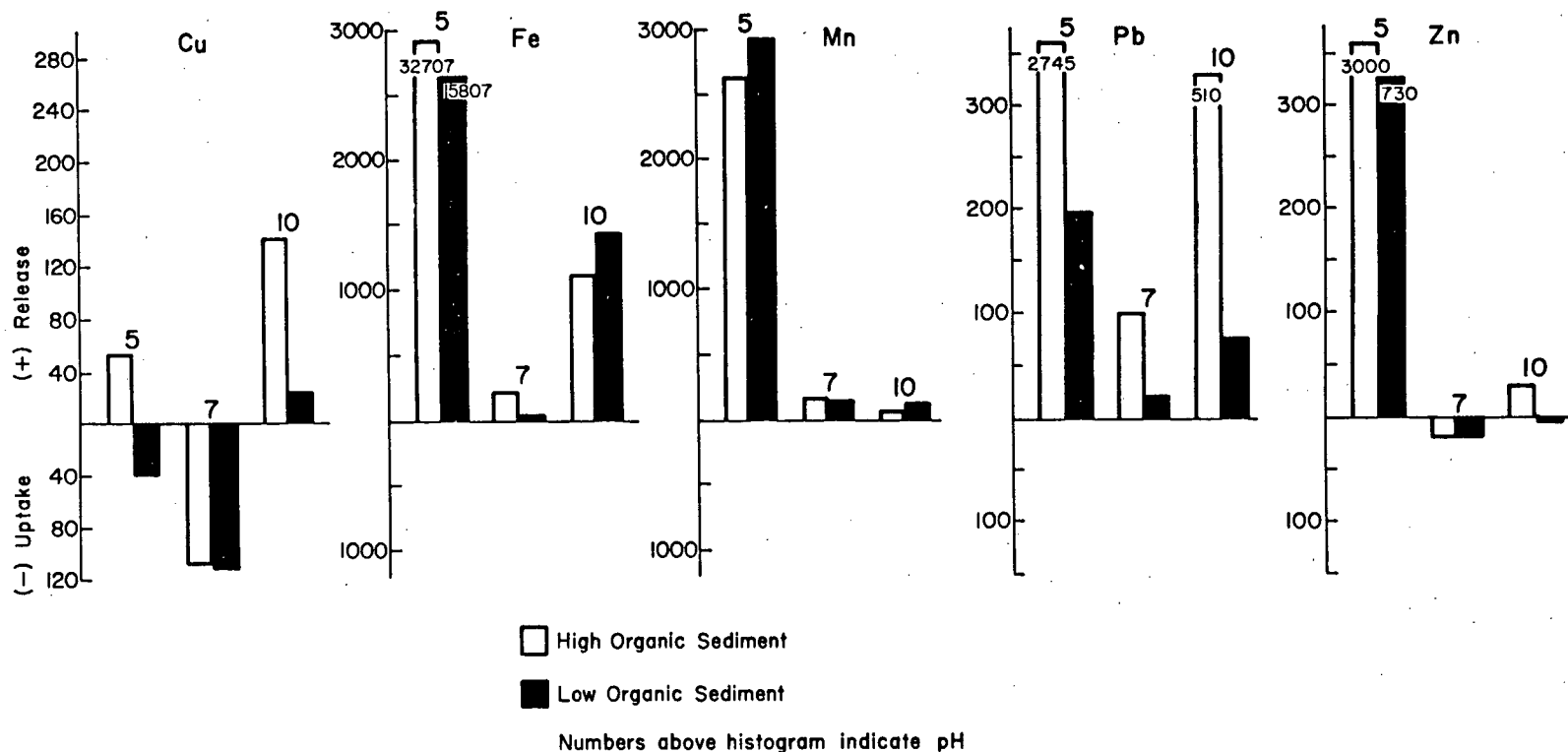
pH 7. The release or uptake of Cu and Zn at pH 5 and 10

varied considerably depending upon the character of the

sediment.

II.   TRACE METAL EXCHANGE BETWEEN SEDIMENTS AND INVERTEBRATES

   A.   Initial Organism and Sediment Trace Metal Levels

        The initial concentrations of total trace metals,

Cu, Fe, Mn, Pb and Zn in the organisms and sediments used in

the exchange experiments microcosms are presented in Table

XII.   The amphipods had very high initial levels of Cu and

Pb reflecting polluted condition of the Squamish River

estuary at the head of Howe Sound (Thompson, 1974).

Similarly, oligochaetes collected from a relatively polluted

area (Ladner sidechannel) of the Fraser River (Hall,

unpublished data) contained high initial concentrations of

Pb and Zn.   The opossum shrimp had the lowest levels of Fe,

Pb and Zn.   The lowest levels of Cu and Mn were observed in

chironomids and amphipods, respectively.

        All total trace metal levels were considerably

higher in the Willingdon Avenue high organic (approx. 7%)

sediment than in low organic sediments (approx. 2.5%)

collected at Gilmore Avenue.   A geochemical distribution of

these 5 metals in sediments collected from the same stations a

few weeks earlier provides some information on their potential

availability to benthic invertebrates (Table X).   The high

organic sediment contained much higher levels of trace metals

Table Xll : Total Trace Metal Concentrations in Organisms and Sediments
Used for Microcosms[1].

Sample	Copper	Iron	Lead	Manganese	Zinc	Comments
Amphipods (Lab., UBC)	162	550	204	23	83.1	Polluted
Chironomids (Ladner Sidechannel near sewage lagoon)	23	5320	35	92	106	
Oligochaetes (Middle of Ladner sidechannel)	27	7130	167	99	147	Polluted
Opossum shrimp (Lab. UBC)	27	383	<8	44	64.9	
Gilmore sediment	129	18300	194	452	108	Low organic matter (2.5%)
Willingdon sediment	356	23500	1280	597	526	High organic matter (6.8%)
Algae[2] (Enteromorpha)	19	3380	7	81	32.5	

1. All values in ppm (mg/kg) dry weight.
2. Food substrate added to amphipod microcosms.
3. Trace Metal Distribution of Ladner Sidechannel Sediment from which
    Oligochaetes were collected (Data from Bindra and Hall, 1977)

Trace Metal	Metal Concentration in Geochemical Fractions (ppm)						
	IW	EP	ERP	OSP	EAEP	RESIDUE	TOTAL (Independent Test)
Copper	<0.02	0.6	<0.3	8.4	27	17	49
Iron	45	7	2070	685	10800	41900	43500
Lead	<0.2	<0.3	<3	6	7	23	22
Manganese	14	28	8	42	178	432	698
Zinc	0.02	0.3	5	9	33	68	121

associated with organic-sulphur phase. Also, considerably higher levels of Pb and Zn were associated with the exchangeable and easily reducible phases in the high organic sediment. In both sediments, with the exception of Fe and Mn, only a small portion of the total trace metals was bound in the residual phase. The low organic sediment (Gilmore) was very sandy with approximately 35% of the material larger than 0.5 mm and approximately 85% larger than 0.25 mm while the high organic sediment (Willingdon) was much finer with over 90% of the material in the very fine sand (0.25 - 0.063 mm) and silt-clay ($<$ 0.063 mm) fractions.

B. Accumulation or Loss of Trace Metals in the Benthic Invertebrates

The changes in concentrations of trace metals Cu, Fe, Pb, Mn and Zn in the aquatic organisms during the exchange experiments are presented in Appendix C (Table C1) and Figure 16.

The opossum shrimp did not live much beyond one week so trace metal levels were only available for this period. Those in the high organic sediment did not even survive for one week. Possibly these organisms are more susceptible to trace metal pollution since they live under a lower trace metal stress as indicated by their initial concentrations of Pb, Fe and Zn. In the low organic sediment, the concentrations of Cu, Fe, Pb and Mn in the shrimp increased by a factor of 3 to 4 during one week.

Figure 16. Trace Metal Levels in Organisms Over Microcosm Period.
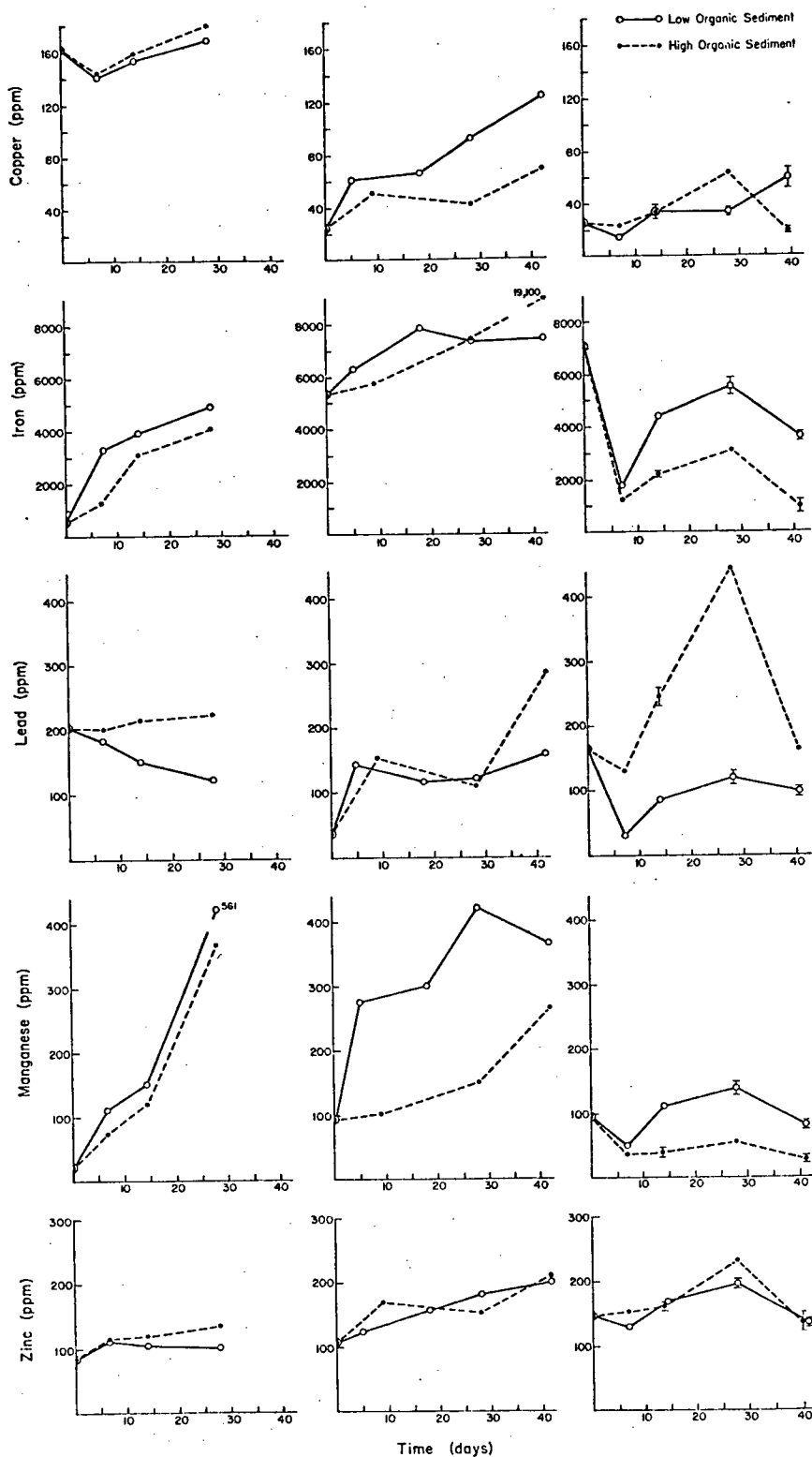
*range of replicate microcosm values

In amphipods, the levels of Fe and Mn increased by a factor of 4 in both sediment microcosms during a four week period. The concentrations of Cu, Pb and Zn in the amphipods did not show much change over the initial levels. There does not appear to be much difference in trace metal exchange from the two different sediments with the possible exception of Pb where organism levels decreased in the low organic sediment while in the high organic sediment the levels remained fairly constant. The trace metal concentrations in the food substrate (Enteromorpha)(Table XII), provided for the amphipods, was probably one of the factors affecting trace metal levels in their tissues. The levels of Fe and Mn, which were the only two elements to show accumulation, were higher in Enteromorpha than in amphipods whereas levels of Cu, Pb and Zn, the elements that did not accumulate in the organisms examined, were lower in Enteromorpha than in the amphipods.

The chironomids showed increases for all five trace metals in the two sediments over the six week microcosm period. There was no consistent trend in accumulation of trace metals from the two different sediments. Both Cu and Mn had consistently higher levels in the organisms in contact with the low organic sediments. Although there was considerable variability between Pb and Fe levels in chironomids in the two sediments, the final concentrations were twice as high in chironomids that were in contact with the high organic sediments. Zinc is another metal for which

the accumulation in chironomids from the two sediments varied during the period of the experiment but unlike Pb and Fe, the final concentrations of Zn in the organisms collected from the two microcosm sediments were similar.

In oligochaetes, the levels of all trace metals dropped from initial values during the first week of the microcosm. This was followed by a general increase in concentrations during the second and third week of the microcosm with a final decrease at the termination of the microcosm. Iron and Mn followed a similar pattern in oligochaetes. Levels of both elements in the oligochaetes in the high organic sediment remained very low while there was a greater attempt to recover to the initial Fe and Mn levels in the low organic sediment. Lead concentrations in oligochaetes in the high organic sediment always remained above levels in organisms present in the low organic sediments although the final concentration was very close to the initial level. The concentrations of Cu and Zn in the oligochaetes did not show any consistent pattern that could be attributed to the sediment used in the microcosm.

Calculations of changes in the concentration ratios of metal in organism / metal in sediment, over the microcosm period, help to normalize the variability of the different initial trace metal levels in the organism and provide a good method to compare accumulation ability among the different organisms for different metals (Table XIII).

Table XIII: Trace Metal Bioaccumulation in Benthic Invertebrates

Trace Metal	Organisms	Initial[1]		Final[2]		Change[3]	
		L	H	L	H	L	H
Copper	Amphipods	1.26	.46	1.30	.51	+.04	+.05
	Chironomids	.18	.06	.71	.12	+.53	+.06
	Oligochaetes	.20	.07	.21	.18	+.01	+.11
	O. Shrimp	.21	-	.67	-	+.46	-
Iron	Amphipods	.03	.02	.21	.22	+.18	+.20
	Chironomids	.29	.23	.40	.32	+.11	+.09
	Oligochaetes	.39	.30	.31	.13	-.08	-.17
	O. Shrimp	.02	-	.05	-	+.03	-
Lead	Amphipods	1.05	.16	.63	.17	-.42	+.01
	Chironomids	.18	.03	.62	.09	+.44	+.06
	Oligochaetes	.86	.13	.63	.35	-.23	+.22
	O. Shrimp	.02	-	.10	-	+.08	-
Manganese	Amphipods	.05	.04	.94	.81	+.89	+.77
	Chironomids	.20	.15	.93	.25	+.73	+.10
	Oligochaetes	.22	.17	.31	.10	+.09	-.07
	O. Shrimp	.10	-	.47	-	+.37	-
Zinc	Amphipods	.77	.16	.93	.26	+.16	+.10
	Chironomids	.98	.20	1.68	.29	+.70	+.09
	Oligochaetes	1.36	.28	1.81	.44	+.45	+.16
	O. Shrimp	.60	-	.64	-	+.04	-

1. Ratio of initial conc. in organism/conc. in sediment.

2. Ratio of final conc. in organism/conc. in sediment after 1 month incubation. For Opossum shrimp time interval = 1 week.

3. Difference between initial and final bioaccumulation ratio, (+) indicates relative increase over sediment concentration, (-) indicates relative decrease over sediment concentration.

L = low organic sediment,   H = high organic sediment.

The amphipods showed a positive accumulation for all metals except Pb in the low organic sediments. The order of accumulation in the amphipods for both sediment types was Mn<Fe<Zn<Cu<Pb. There was very little variability in concentration ratio changes for the two different sediments suggesting that the trace metals in the Enteromorpha may have influenced accumulation.

Chironomids showed an increase in concentration ratios for all trace metals. There was a much greater increase in the concentration ratios of all metals in the low organic sediment. With the exception of Fe, changes in the concentration ratios were 7 to 8 times higher for the low organic sediment than for the high organic sediment.

Oligochaetes showed considerable variability in their ability to accumulate trace metals. There was an increase in accumulation ratio for Cu and Zn in both sediments, whereas the ratios for Fe decreased. Lead and Mn showed a variable change in accumulation ratio depending upon the sediment.

Opossum shrimp showed an increase in the accumulation ratio for all metals in the low organic sediments. The largest increase was for Cu and Mn with only small changes for Fe, Pb and Zn.

C. Rate of Uptake or Loss of Trace Metals by Benthic Invertebrates

The changes in trace metal levels in the benthic invertebrates over the one and two week intervals spanning

a 28 day period of the microcosms as shown in Appendix C
(Table C) were used to calculate the rate of uptake or loss
of the metals in the organisms for each time interval. The
uptake rates for individual intervals were used to obtain
average rates over the 28 day period. The averaged results
expressed in mg/kg dry weight/day are presented in Table XlV
with standard deviations in parentheses. The negative sign
denotes a loss.

The uptake rate calculations were limited to a 28
day period although chironomid and oligochaete microcosms
spanned a period of 42 days. This was considered appropriate
for comparisons of uptake results between different species.

Amphipods showed the highest uptake rates for Fe
and Mn followed by chironomids and the amphipods had the
smallest of the rates for Cu and Zn. These relative rates
were consistent for both the high and low organic sediments.
The uptake rates of Cu and Pb for amphipods in contact with
the low organic sediment were negative indicating that the
metal was being lost by the organisms over the 28 day period.
With the exception of Zn, chironomids showed a higher uptake
rate in the low organic sediment. Chironomids had the highest
uptake rates for Cu and Zn followed by oligochaetes in contact
with both the low and the high organic sediments. Except for
Mn from low organic sediments the oligochaetes' uptake rates
of Fe and Mn were negative indicating that the metals were lost
by the organism over the 28 day period. The uptake rate of Mn
by oligochaetes from the low organic sediment was positive but

Table XIV: Average Uptake Rate of Trace Metals by Benthic Invertebrates[1] (0-28 days).

Trace Metal	Organism	High Organic Sediment Average (S.D.)	Low Organic Sediment Average (S.D.)
Copper	Amphipods	0.33(3.9)	-0.033(3.8)
	Chironomids	1.34	3.53 (5.29)
	Oligochaetes	1.05(1.75)	0.38 (3.26)
Iron	Amphipods	143(150)	183 (254)
	Chironomids	68	92 (133)
	Oligochaetes	-212(767)	-101 (937)
Lead	Amphipods	0.67(2.10)	-3.25 (1.84)
	Chironomids	5.37	6.67 (18.4)
	Oligochaetes	8.59(16.73)	-2.92 (20.6)
Manganese	Amphipods	10.45(8.82)	16.05 (15.93)
	Chironomids	1.79	16.9 (25.1)
	Oligochaetes	-2.33(7.82)	1.31 (11.14)
Zinc	Amphipods	2.09(3.06)	0.93 (3.78)
	Chironomids	3.02	2.81 (0.72)
	Oligochaetes	2.41(3.28)	1.71 (5.66)

1. Values expressed as mg/kg dry wt. of organism/day.
    Negative values indicate a net loss of metal.
    S.D. = Standard Deviation
    n = 3, except for chironomids in high organic sediment
    microcosms for which n = 2

smallest of the rates for the three species examined. However, because of the large variability in uptake rates as indicated by standard deviations the differences in uptake rates do not appear to be significant. Purely on the basis of statistics, it is possible to miss the importance of the results. As depicted in Figure 16 the variation in uptake rates between successive intervals reflects dynamics of trace metal uptake and control mechanisms.

D. Reproducibility of Trace Metal Determination in Organisms

Analysis of oligochaetes from duplicate microcosm chambers containing similar sediments and harvested on the same day are presented in Table XV. There was insufficient space and numbers of organisms to set up duplicates for each organism at each time interval. However, the four duplicate sets of oligochaetes provide some estimate of biological variability and analytical precision. The percent variation in the two values of each replicate relative to their mean value is summarized in Table XVl.

Manganese showed the greatest variability with an average of 24.8 percent between replicates with a high value of 41.2 percent. The average reproducibility of Fe, Pb and Zn was within 8 - 11 percent of the mean, while Cu values had an average difference of 19 percent.

Table XV : Reproducibility of Trace Metal Determinations in Oligochaetes from
Replicate Microcosm Chambers[1].

Sampling Date and (Sediment)	Bioassay Chamber	Copper	Iron	Lead	Manganese	Zinc
June 14, 1978 (High Organic Sediment)	1	29.4	2310	235	35.3	155
	2	39.1	2140	261	48.4	169
July 12, 1978 (High Organic Sediment)	1	19.4	789	168	39.0	155
	2	21.6	829	168	26.5	123
June 28, 1978 (Low Organic Sediment)	1	31.9	5200	112	150	203
	2	37.1	5890	133	130	190
July 12, 1978 (Low Organic Sediment)	1	53.2	3490	92.4	88.6	133
	2	67.0	3820	108	78.0	140

1. All values in ppm (mg/kg dry wt.).

Table XVI : Percent Variability in Trace Metal Levels in
Four Duplicate Oligochaetes Microcosm.

Trace Metal	Percent Variability	
	Average	Range
Cu	19.1	10.7 - 28.3
Fe	8.4	7.6 - 12.3
Mn	24.8	12.7 - 41.2
Pb	10.7	0.0 - 17.7
Zn	10.8	5.1 - 23.0

Chapter 4

DISCUSSION OF RESULTS

I. GEOCHEMICAL PHASES

It has recently been recognized that to fully assess impact of trace metals on water quality and aquatic organisms, exact knowledge of the metals' association with various mineral phases of the sediments is necessary (Kitano et al., 1980). The bulk chemical composition of sediments is a poor indicator of environmental significance of trace metals in sediments (Serne, 1975). As a result, a half dozen different extraction schemes have been developed (Tessier et al., 1979). A modified version of the scheme proposed by Engler et al., (1974) was chosen for this study. This scheme is designed to provide a realistic representation of actual trace metal and mineral associations, for sediments are kept in their original physical and chemical state as much as practically possible[1]. Following is a brief discussion of the various geochemical phases obtained by the extraction scheme employed in this work.

A. Interstitial Water (IW)

Interstitial water is water in sediment pores which is in dynamic equilibrium with various mineral and organic components of the sediment. Trace metals in interstitial

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1. Since fresh sediments were used for geochemical extractions but frozen sediments for exchange experiments, the relationships between trace metal exchange and their geochemical distribution as discussed in this chapter should be viewed keeping in mind that geochemical distribution of metals in sediments can change in freezing (Thomson et al. 1980, Water, Air and Soil Pollution, 14 , 215-233).

water may diffuse to overlying water or may be released during dredging operations (Chen et al., 1976). The interstitial fraction of trace metals may also be accumulated by burrowing tubificid worms (Guthrie et al., 1979). Chemistry of IW in Saanich Inlet, British Columbia, was investigated by Presley et al. (1972).

B.   Exchangeable Phase (EP)

EP is that portion of trace metals in sediments which is bound to sediment particle surfaces through adsorption from water. Exposure of sediments to salt waters as it occurs at river-estuary interface may result in release of the exchangeable phase of trace metals by replacement action of Na^+, K^+, Ca^{2+}, Mg^{2+} ions (Kharkar et al., 1968). In the laboratory EP phase may be extracted with NH_4OAC, or other similar chemicals (dilute HCl, $NaCl$, $MgCl_2$, etc.).

C.   Easily Reducible Phase (ERP)

ERP extract represents trace metals held in Mn oxides, some amorphous Fe oxides and carbonates. Under reducing conditions this phase of trace metals may be relatively easily mobilized (Jenne, 1968; Leeper, 1972). Chao (1972) proposed a method for selective isolation of this phase of trace metals from soils and sediments.

D.   Organic and Sulphur Phase (OSP)

Trace metals bound to organic compounds and sulphides oxidizable with hot acidified H_2O_2 comprise the

OSP phase. Under oxidizing conditions, as may occur in the case of disposal of anoxic, contaminated dredged sediments on land, the OSP phase may become unstable and be leached out in storm runoff. Jackson (1958) recommended the use of hydrogen peroxide digestion for determining the concentration of soil OSP nutrient trace metals.

E.   Easily Acid Extractible Phase (EAEP)

Trace metals contained in metamorphic crystalline Fe oxides constitute the EAEP phase. EAEP trace metals may mobilize in a persisting anoxic environment or under acidic conditions. This phase of trace metals is relatively more tightly held in sediments than the previously discussed phases. Engler et al.(1974) proposed the use of a method first suggested/used by Holmgren (1967) for soils. Recently Malo (1977) recommended a new method which proved to be equally efficient and selective for isolation of iron oxide associated trace metals but without presenting some of the analytical difficulties associated with the Holmgren's approach (see chapter 2).

F.   Residue Phase (RP)

This phase represents the fraction of trace metals tightly bound in silicate minerals. Only a harsh chemical treatment such as digestion in hot $HF-HNO_3$ acid mixtures can free this fraction of trace metals from sediments. This phase has been found to contain the largest fraction of trace

metals in sediments (Serne, 1975) and the fraction decreases where trace metals in sediments accumulate from anthropogenic sources(Tessier et al., 1980). This phase is least important from an environmental point of view.

G.   Total Phase (Total)

Determination of total concentrations requires a chemical digestion similar to that discussed for the residue phase (RP). Only a fraction of the total trace metals may affect the aquatic environment; therefore, the importance of total trace metal concentrations has been questioned (Gupta and Chen, 1975).

II.   TRACE METAL EXCHANGE AT SEDIMENT-WATER INTERFACE

A.   General

1.   Static columns

The static column laboratory tests were used to simulate relatively quiescent field conditions in which the trace metals are present in sediments where very little resuspension occurs but where possible change in overlying water chemistry could affect exchange reactions. Changes in water chemistry could result from stratification with associated oxygen depletion and pH reduction that often occur in eutrophic lakes,or from tidal salt wedge penetration in an estuary.

Static column laboratory experiments have been conducted by other researchers to investigate sediment

exchange reactions under conditions of minimum sediment disturbance (Fillos and Swanson, 1974; Stokes and Szokalo, 1977; Lu and Chen, 1977; Leudtke and Bender, 1979; Bothner et al., 1980).

2. Elutriate tests

The elutriate test simulated exchange reactions between sediment and water. These could occur under natural conditions where high surface runoff results in sediment suspension. Also man-induced activities such as dredging, pile driving and shipping in shallow channels can result in sediment disturbance and resuspension which could affect metal exchange reactions (Windom, 1975; Lee and Mariani, 1977; Chen et al., 1976; Wakemann, 1977). Physical disturbance of sediments is a well documented phenomenon (Rhoads, 1963; Gordon, 1966; Jones and Bowser, 1978) which could also imbalance the normal equilibrium state of the sediment-water interface and thereby influence trace metal exchange (Robbins and Edington, 1975; Aller and Cochran, 1976; Schink and Guinasso, 1977; Leudtke and Bender, 1979).

Trace metal exchange in elutriate tests was different from exchange in column tests in some ways. In elutriate tests, exchange was rapid in the sense that sediment and water were exposed to each other extensively and immediately but severely hindered because of lack of time for chemical and biochemical (bacterial) reactions to approach an equilibrium state. In contrast, although physical exchange

for columns was slow as it depended upon diffusion of water in and out of the sediment layer, sediment and water (interstitial water) were in contact for long enough times to undergo diagenetic reactions involving transfer of trace metals. These differences should be considered in comparing exchange results between the elutriate tests and the column studies.

B. Dissolved Trace Metal Exchange

Initial set up of columns resulted in the release of dissolved metals from resuspended sediments. However, values soon decreased reaching equilibrium after 2 to 5 days. The initial release of metals probably resulted from introduction of metal-rich sediment pore water into the water layer. Fillos and Swanson (1974) also reported high initial concentrations of Fe and phosphorus during experiment initiation, which they attributed to disturbance of sediment. Similarly high initial release of Mn was observed by Graham et al. (1976) in their in situ chamber studies in Narragansett Bay. Graham et al. attributed the high initial release of Mn to introduction of pore water as the sediment was disturbed in the chambers during emplacement. Therefore, the initial release of metals from resuspension of sediments seems to be a common problem in setting up quiescent systems even though extreme care is exercised.

Results of dissolved trace metal exchange studies carried out in column microcosms and using the elutriate test

procedure are discussed below taking one metal at a time.

1. Copper (Cu)

In column studies, during freshwater equilibrium dissolved Cu in the low organic system under both oxic and anoxic conditions (see footnote p. 89) reached equilibrium values of approximately twice those found in the high organic system even though both sediments contained similar total Cu and had a similar geochemical distribution of Cu. The higher Mn, Fe and organic matter content of the Willingdon sediment most likely limited release of Cu into solution. Means et al. (1978) have shown that oxides of Mn and Fe and organic matter have adsorptive capacities for trace elements which could result in lower equilibrium concentrations in overlying waters. A field study by Lopez and Lee (1977) indicated similar profiles of Cu, Fe and Mn in Torch Lake, Michigan, sediments which supports the belief that Fe and Mn may deposit Cu in freshwaters. Sanchez and Lee (1978) observed lower values for dissolved Cu in Lake Monona, Wisconsin. Low Cu levels in the hypolimnetic anoxic layer were attributed to lower solubility of Cu sulphide, but carbonate was believed to be controlling solubility in the aerobic epilimnion layer. In this study inorganic carbon in sediments was low , so Cu carbonate probably was not regulating solubility. Also, production of Cu carbonate during the experiment could not be significant because constant purging by nitrogen or air prevented accumulation

of carbon dioxide (Khalid et al., 1978). In the freshwater
systems of this study, the organic carbon (8-19 mg/l) was
probably more important in regulating dissolved Cu levels
through complexation and / or through influence on adsorption-
desorption reactions. Payne and Pickering (1975) have
demonstrated that ligands such as acetate and tartrate can
greatly influence the adsorption of Cu to clay. Presence of
NTA-like ligands may also control levels of Cu in freshwater
systems (Sanchez and Lee, 1973). The two types of sediments
used in the present study also differed in particle size.
Wolfberg et al. (1980) believe that high organic soils or
clayey soils could remove Cu to a greater extent than the
sandy soils. Results of Lu and Chen (1977) confirm this,
belief in that Cu was more readily released from their sandy
sediment than from their clayey sediment.

In freshwater elutriate tests, Cu was completely
removed regardless of organic matter content, oxygen
conditions or Cu concentrations in sediments. Since Cu in
solution is exposed to large mineral surface areas, the metal
was readily removed (O'Connor and Kester, 1975) and differ-
ences in geochemistry of the sediments or chemistry of
water were superseded.

In column studies, during the first salinity
adjustment in the aerobic system there was some release of
Cu into solution especially in the high organic column.
This is attributed to desorption of Cu from the sediment

as it has been observed in the Rhine Estuary (Groot et al., 1976) and in the Fraser Estuary (Thomas and Grill, 1977); in the former case up to 80 percent Cu was released as sediment was transported through the estuary. In a coastal environment, Menon et al. (1979) also observed similar Cu desorption from sediments and the authors believe that cations Ca^{2+} and Mg^{2+} in the seawater were exchanged for Cu ions. A greater release from the high organic sediment can be explained by the results of Rohatgi and Chen (1975) where Cu among some other trace metals was removed from sewage related organic solids on suspension in seawater in the presence of dissolved oxygen. The removal of the metals from the organic solids was believed to have occurred due to oxidation of organic matter and simultaneous release of associated trace metals. Free metal ions in seawater are probably stabilized in solution by formation of coordinate complexes with various anions, OH^-, Cl^-, CO_3^{2-}, HCO_3^- and SO_4^{2-} (Long and Angino, 1977). The high organic sediment also contained slightly more Cu in the OSP phase. Although the EAEP phase of the high organic sediment contained twice as much Cu as this phase in the low organic sediment because of greater stability of crystalline iron oxide under aerobic conditions, the greater release of Cu from the high organic sediment could not be attributed to this difference in geochemistry of the metal.

In elutriate tests, Cu was removed from solution under both oxic and anoxic conditions over a wide salinity

range even though Cu concentrations in the sediments used
in these tests were several times greater than the
concentrations for the sediments used in the column studies.
Aeration of the sediment-water mixture over a 30 minute period
for the high organic sediment obviously was not sufficient
to break down (oxidize) organic matter as observed by
Rohatgi and Chen (1975) and Lindberg and Harriss (1977).
Removal of Cu from seawater by freshwater sediments in
elutriate type tests has been observed elsewhere (Wagemann
et al., 1977; Gustafson, 1972; Lee et al., 1975). The
removal was most likely due to adsorption of Cu on surfaces
of sediment particles. Precipitation of Cu could also occur
but through different mechanisms for oxic and anoxic tests.
Lee et al. (1975) showed that under oxic conditions dissolved
Fe from IW phase of sediment oxidizes and precipitates and
in the process removes other trace metals from solution.
Under anoxic conditions formation of low solubility Cu
sulphide may result in removal of the metal (Okutoni and
Okaichi , 1971). Oakley et al. (1980) showed that under
anoxic conditions Cu preferentially binds to Fe sulphide.

Under oxic conditions at full seawater strength
(S=25-30 ^{o}/oo) both in quiescent (column) and elutriate
studies there was some release of Cu from both sediments.
It seems that forces responsible for Cu removal as discussed
previously were eventually overcome by increasing
concentrations of exchange cations Ca^{2+} and Mg^{2+} and
complexing anions such as chloride and hydroxide. In

elutriate tests where surface reactions of metal removal from solution can be more effective, slightly less Cu was released from the high organic fine sediment. In column studies where exchange of water through sediment pores may control exchange rates, greater Cu release was measured from the coarser low organic sediment.

In the pH studies, both in microcosms and elutriate tests, dissolved Cu levels were generally higher in the high (10) and low (5) pH systems than that at the natural pH (approx. 7). In the low pH systems, acetate was used as a buffer which could aid in desorption of Cu from the sediments (Payne and Pickering, 1975) and keep it in solution as an acetate complex although metal speciation was not determined. Under acidic conditions carbonates, oxides and hydroxide mineral phases of sediments react with protons and dissolve in water releasing the associated trace metals in the process. A number of geochemical phases namely EP, ERP, OSP and EAEP are unstable under low pH conditions and hence must have contributed to trace metal release at pH 5.

Trace metal release under low pH conditions has been measured by others. Naumov et al. (1972) measured dissolved Cu concentrations in the range of 26.6 - 153 mg/l in the ore waters of Cu - Bi deposits where pH ranged from 3.05 - 4.25. Stokes and Szokalo (1977) also observed that release of Cu and Ni from sediments placed in laboratory aquaria was related to a decrease in pH of the overlying water.

In the high pH systems, carbonate buffer should control the dissolved Cu at a low concentration as measured by Sanchez and Lee (1978) in Lake Monona, Wisconsin. Theoretical calculations of Zirino and Yamamoto (1972) suggest that at pH 10 $Cu(OH)_2$ would be a dominant species and therefore control the solubility of Cu. However, high pH also solubilized organics from the sediment (TOC=50 mg/l and color=500 mg/l Pt.). These humic-like organic substances have a high complexing capacity for Cu and other trace metals (Schnitzer and Skinner, 1967; Cheshire et al., 1977; Reuter and Perdue, 1977). Kunkel and Manahan (1973) discuss how chelating agents can stabilize cupric ions in solution at pH 10 by forming multiligand coordinate complexes with the metal. Results of a study by Bondarenko (1972) are particularly interesting in relation to the present study. Humic and fulvic acids were used to dissolve Cu in concentrations up to 26.25 mg/l under alkaline conditions. Solutions at initial pH values from 10 to 11 were unstable over a period of 510 days; both dissolved Cu and pH values dropped over the 510 day period. The concentrations of dissolved Cu were still in the 10 to 20 mg/l range.

In the pH studies, the high organic sediment when subjected to low (5) and high (10) pH conditions released more Cu into solution than did the low organic sediment. The greater release from the high organic sediment can be

attributed to differences in Cu distribution between the two
sediments and their geochemical phases. The high organic
sediments used in the pH studies were collected from Still
Creek about 4 months after the low organic sediments
(Table IX and X). During the intervening period trace metal
(Cu, Pb and Zn) concentrations in the sediments increased.
Therefore, Cu levels in the high organic sediment were
almost 5 times those in the low organic sediment. The
presence of more Cu in the high organic sediment could have
resulted in a greater release of the metal from this sediment.
Copper in the ERP, EP and IW probably accounts for most of
the release at low pH (Chester and Hughes, 1967). The three
geochemical phases ERP, EP and IW of the high organic
sediment together contained 9 times more Cu than the total
for the three phases in the low organic sediment. At high
pH (10), dissolution of organic matter occurred and since
over 200 ppm Cu was bound to the OSP phase of this sediment
(Table X), high dissolved Cu concentrations were obtained.
This Cu would be stabilized in solution by association with
humic-like substances as discussed previously.

2. Iron (Fe)

Iron in the oxic freshwater columns reached
equilibrium concentrations of approximately 75 μg/l.
Koenings (1976) in a study of Fe in an acid-bog lake

calculated that dissolved iron in an oxygenated system at neutral to basic pH should not exceed 17 μg/l. Iron concentrations in rivers far exceed the concentrations calculated from equilibrium relationships involving inorganic reactions (Stumm and Morgan, 1970; Jones et al., 1974). Co-occurrence of high concentrations of dissolved Fe and organic matter has been observed by many authors (Abdullah and Royale, 1972; Perdue et al., 1976; Moore et al., 1979). Organic substances are believed to cause high concentrations of Fe in oxic waters by either forming chelate type of complexes with the metal ions (Perdue et al., 1976) or adsorption on inorganic ferric hydroxide colloids (Hem and Cropper, 1959). Adsorption of organics enhances stability of Fe colloid suspensions. Under the oxic conditions of the columns in this study probably the latter mechanism was predominant. The colloid particles could readily pass through the 0.45 μm size membrane filters used in obtaining samples for dissolved metal analyses (Hem, 1972).

In oxic elutriate tests at near freshwater conditions (Salinity $<$ 4 ^{o}/oo) there was some release of Fe especially from the low organic sediment. A greater release of Fe from the low organic sediment may be attributed to desorption of its poorly adsorbed abundant exchangeable phase (Table X). At higher salinities, however, desorption was accompanied by coagulation of colloidal Fe, the form in which filtrable Fe occurs at slightly alkaline pH values. Edzwald

et al. (1974) studied the stability of particulate suspensions in estuarine water of varying salinity (0-16 ^{o}/oo). Stability of colloids sharply drops in the salinity range of 2 to 4 ^{o}/oo. Iron flocculation in estuaries has been studied by Coonley et al. (1971), Boyle et al. (1977) and Sholkovitz (1976).

In column studies, the first salinity change, achieved by replacing half the existing freshwater with seawater, resulted in a large salinity increase from zero to 14.5 ^{o}/oo. Under oxic conditions dissolved Fe concentrations dropped below the 10 μg/l level. As in the elutriate tests, this can be attributed to coagulation of ferric hydroxide colloids.

Under anoxic conditions there was a considerable release of Fe from both sediments in the elutriate tests and from the low organic sediment in the column studies. Under anoxic conditions, release of Fe from sediments has been observed in other studies. Patrick et al. (1973) found that strengite ($FePO_4$. $2H_2O$) incubated in water under low redox and low pH conditions underwent maximum dissolution. In a laboratory microcosm, Fillos and Swanson (1974) measured significant release of Fe and phosphate when water above the sediment was made anoxic. Mortimer (1941) found that Fe and Mn were not released until dissolved oxygen values dropped below 2 mg/l. In a laboratory study, Chen et al. (1976) also measured considerable release of Fe (maximum 1.95 mg/l) from sediments to water adjusted to low redox conditions by

purging with nitrogen gas. In elutriate tests Lee et al.
(1975) obtained identical results. Under anoxic conditions
Fe concentrations in the elutriate were up to 7 mg/l whereas
under oxic conditions the values did not exceed the 0.048 mg/l
level for the Corpus Christi Bay sediments. Under anoxic
conditions the ERP phase of sediments is unstable and hence the
most likely source of measured release of Fe under these
conditions.

With respect to Fe release under anoxic conditions,
the two sediments behaved differently. In column studies
under anoxic conditions Fe levels dropped to the detection
level (<1 μg/l) in the high organic sediment while as
discussed above there was a substantial release of the metal
from the low organic sediment. The water quality conditions
in these two anoxic systems do not provide an explanation for
the large differences in Fe release. Therefore, the
geochemistry of Fe in the sediment must be the important
regulating factor. It appears that the Willingdon sediment
with the higher organic content and finer particle size was
able to prevent the release of Fe into solution even though
it had a higher total Fe level and higher levels in the more
labile phases (EP and ERP). Also, the high organic sediment
may have precipitated more Fe as FeS, inhibiting further
release. Free sulphides which are produced under anoxic
conditions in the sediments react with the available Fe to
form characteristic black FeS deposits (Berner, 1969). Such

deposits are commonly observed in reduced lacustrine sediments (Jones and Bowser, 1978). In this study, coincident with the drop in Fe levels in the Willingdon sediment under freshwater conditions was the appearance of a black color characteristic of FeS on the surface of the sediment. The black color of the sediment surface for the high organic microcosm system persisted throughout the subsequent salinity changes. No such black coloration of the low organic sediment was observed. In the elutriate tests, due to lack of sufficient time for production of hydrogen sulphide, subsequent inhibition of Fe release was not possible.

Iron released from the low organic sediment was less stable at higher salinities probably because there was less dissolved organic matter to stabilize its colloids in water (Hem and Cropper, 1959).

In the variable pH microcosms and elutriate tests, the greatest Fe release occurred at pH 5 which is consistent with observations of Patrick et al. (1973). High release of Fe at pH 5 is easily understandable because at such a low pH hydrous oxides of Fe and carbonates are unstable (Gupta and Chen, 1975; Chester and Hughes, 1967). At pH values of 6 or higher the solubility of ferric hydroxide should control Fe in solution at very low levels (Koenings, 1976). Lewis (1977) studied the effect of acidic mine drainage on the ^{210}Pb concentrations in the water of the West Branch of the Susquehanna River (WBSR) ; he noted that ^{210}Pb, Fe and Mn

were precipitating out of solution as pH was rising from less than 4 to 7 as a result of alkaline discharges downstream from the point of the mine drainage entry.

Release of Fe at high pH (10) systems was obviously attributable to association with humic-like organic compounds in carbonate-bicarbonate buffer (Shapiro, 1964). According to Shapiro (1964) mobilization of Fe at high pH and redox potential is due to formation of chelate type soluble complexes (Hutchinson, 1957; Stumm and Morgan, 1970). Also, Shapiro (1964) has shown that Fe holding capacity of yellow organic acids separated from aquatic sediments was maximum at pH 10 in the pH range of 5 to 11 tested. Ferric iron, which is dominant under oxic conditions, has been shown to form stronger bonds with humic acids than Fe^{2+} (Stumm and Lee, 1960; Sensi et al., 1977).

In microcosm pH studies, Fe release from the high organic sediment was generally greater than the Fe release from the low organic sediment. Since water chemistry, due to the use of identical buffer systems, was similar the differences in metal release can be only attributed to differences in sediment geochemistry and physical characteristics. The high organic sediment used in pH microcosms (Table X) contained several times more Fe in IW, EP, ERP, OSP and EAEP phases than in the same phases in the low organic sediment (Table IX). Hence it is not surprising that Fe release from the high organic Willingdon sediment

was greater at pH 5, 7 and 10. Low permeability of this fine sediment deposit was more than offset by greater geochemical availability of the metal.

A greater release from the high organic sediment at pH 5 can be similarly explained by a greater amount of Fe in geochemical phases (IW, ERP, OSP and EAEP) of the high organic sediment.

In elutriate tests, a greater release of Fe at high pH (10) from the low organic Gilmore Avenue sediment containing lower OSP phase Fe levels (Table X) is a surprising result. The substantially greater EP phase Fe levels of the low organic sediment together with differences in physical characteristics such as particle size distribution and differences in chemical nature of organic matter content may account for this result.

3. Lead (Pb)

In microcosm studies, dissolved Pb rapidly dropped to equilibrium concentrations of less than 10 μg/l in both freshwater oxic and anoxic systems. My data accord with those of Hem and Durum (1973). They predicted an equilibrium solubility for Pb of 10 μg/l at pH of 8 with total carbonic species of 10^{-3}M. According to Saar and Weber (1980)

certain types of organic materials may limit the concentration of Pb ions by co-precipitation. Conditional stability constants for river water humic acids (WHA) determined by Buffle et al. (1977) at near neutral pH values are: Pb-WHA, pH=6.7, $-\log \beta_1 = 6.0$, Pb-WHA, pH=6.8, $-\log \beta_1 = 5.5$; Pb-(WHA)$_2$, pH=6.8, $-\log \beta_2 = 10.4$. Based on data from Buffle et al. and their own experiments, Saar and Weber (1980) believe that Pb-WHA or Pb-(WHA)$_2$ co-precipitation in freshwater, where Pb concentrations seldom exceed 2.4×10^{-7}M and humic substance (MW=1000) concentrations typically are 10^{-6} to 10^{-4}M, is not likely to occur. At low concentrations of Pb, adsorption is more likely the mechanism of removal. Under freshwater conditions adsorption was rapid by the high organic sediment which had greater exchange capacity for Pb as indicated by the exchangeable amount of the metal present in the sediment (Tables IX and X). This sediment also contained higher easily reducible phase Fe precipitate which is known to scavenge trace metals like Pb by surface action. The low organic sediment contained more ERP Mn; it appears that the higher ERP Mn in the low organic sediment was not sufficient to offset the effect of greater ERP Fe in the high organic sediment.

Under slightly saline conditions in elutriate tests and after the first salinity change in microcosms, Pb was released from the sediments. Metals adsorbed by sediments under freshwater conditions may be desorbed

under saline conditions due to exchange reactions of Na^+, Ca^{2+}, and Mg^{2+} cations and complexing reactions of anions like Cl^- and OH^-. Desorption of trace metals from sediments in saline waters has been observed by others (Kharkar et al., 1968; Troup and Bricker, 1975; Ramamoorthy and Rust, 1978; Revitt and Ellis, 1980). According to Biggins and Harrison (1980) Pb colloids deposited from automobile exhaust may be resuspended in water and pass through 0.45 μm membrane filters (Hem and Durum, 1973) and hence be measured as dissolved Pb. Net effect of increasing salinity and pH may be removal of dissolved Pb. After the second salinity change in microcosms (24.5 ^{o}/oo) and at salinity of 4 ^{o}/oo in elutriate tests, Pb was removed to below detection levels. As Edzwald et al. (1974) have shown, increasing salinity was probably coagulating Pb colloids. Poor desorption of Pb from sediments suspended in saline waters has also been observed elsewhere (Benninger et al., 1975; Wagemann et al., 1977; Scott, 1980).

The release of Pb measured in oxic static columns at a salinity of 14.5 ^{o}/oo was not observed in elutriate tests. Perhaps the kinetics of Pb desorption and/or complexation are slow and a longer equilibrium time is required to bring Pb into solution. Four days were required before Pb was measured in the column at 14.5 ^{o}/oo salinity. Similar slow release was measured by Chen et al. (1976) and Khalid et al. (1978) in their desorption experiments under oxic conditions.

Lead associated with sewage solids was less mobile under brackish conditions than some other metals (Rohatgi and Chen, 1975). Most Pb in the sediments used in the present study was bound to OSP phase (Tables IX and X).

In the elutriate tests more Pb was released from the high organic sediment under slightly saline conditions. Since desorption is a surface phenomenon, the finer particle size of the higher organic sediment may have been a factor in the higher release of Pb from this sediment.

Under anoxic conditions Pb was not released into solution under different salinity regimes. Identical results were obtained by Lu and Chen (1977); dissolved Pb at the sediment-seawater interface remained in the sub ppb (μg/l) range during a 30 day period. This result was independent of sediment type (silty-clay, sandy-silt or silty-sand). Under reducing conditions, particularly in the long- term static column experiments, sulphide precipitation of metal ions probably inhibited Pb release (Bella, 1972; Hem and Durum, 1973; Engler and Patrick, 1975). The ERP phase of the low organic sediment contained about 6 times more Pb than the corresponding phase of the high organic sediment (Table IX). Since Pb release was not measured from either one of the two sediments, it suggests that sulphide precipitation overwhelmed any release of Pb from dissolution of the ERP phase.

In the variable pH studies, high concentrations

of Pb were released at the low (5) and the high (10) pH

systems. Results obtained from static columns were confirmed

by the elutriate studies. Geochemical fractions from IW to

EAEP ,containing over 80 percent of Pb (Tables IX and X) ,are

unstable under acidic conditions and tend to dissolve. Hence

it is not surprising that maximum dissolution occurred at

the lowest pH (5). At pH 5 hydrolysis of Pb is at a minimum

(Hahne and Kroontje, 1973) and hence other species in water

such as organics and carbon dioxide may be controlling the

Pb concentrations. According to thermodynamic calculations

of Hem and Durum (1973) at a low concentration of carbonic

species $(10^{-3}M \ CO_2)$, at pH 5 Pb concentration in water may

reach as high as 1000 mg/l. Henderson et al. (1979) leached

Pb from ceramics up to concentrations of over 100 mg/l

depending upon the amount of Pb used in glazing. The leaching

agent was a 5 percent solution of acetic acid. Patrick et al.

(1977) and Day et al. (1979) also measured considerable

release of Pb from sediments and street dusts respectively.

Day et al. (1979) argue that a greater solubility of Pb at

low pH and oxic conditions is not unreasonable because both

carbonates and sulphates of the metal convert to soluble

bicarbonates and bisulphates respectively and adsorbed Pb

ions exchange for abundant hydrogen ions. The most likely

source of Pb in the sediments was automobile exhaust

(Hall et al., 1976) which is emitted mainly in carbonate

(ERP) and sulphate (ERP) forms (Motto et al., 1970; Daines

et al., 1970; Biggins and Harrison, 1980; present study,
Tables IX and X).

Concentrations of Pb at pH 5, however, were much
lower than the value of 1000 mg/l suggested by calculations
of Hem and Durum (1973). The maximum dissolved Pb
concentration of approximately 2.7 mg/l was measured in the
elutriate of the high organic sediment. Under quiescent
conditions dissolved Pb concentrations were lower probably
because of poor contact between the acidic overlying waters
and the sediments. Discrepancies between the theoretical
calculations and the measured values may be accounted for
by the presence of other species such as acetate ion and
natural organic compounds which were not taken into consider-
ation by Hem and Durum (1973) in their calculations. Payne
and Pickering (1975) have shown that the presence of organic
compounds may affect the adsorption/desorption behavior of
metal ions.

A high release of trace metals at as low a pH as 5
is a common observation and a readily acceptable result ,
whereas a high release at pH 10 is a somewhat unexpected
observation, although similar observations have been made
elsewhere (MacPherson et al., 1958; Hakanson, 1974). As
discussed earlier for Cu and Fe, a high release of Pb and
other trace metals at pH 10 may be attributed to dissolution
of humic-like substances carrying the metal ions (Desai et
al., 1972; Cooper and Harris, 1974). A considerable portion
of the total Pb in the sediments was in the organic and

sulphur phase (Tables IX and X). Both low pH (5) and high pH (10) release of Pb from the Willingdon sediment were considerably greater than release at neutral pH. This can be easily explained by the differences in concentrations of Pb in the geochemical fractions of the sediments (Tables IX and X). For static column tests the Willingdon sediment contained approximately 6 times more total Pb, 15 times more Pb in EP and ERP (readily soluble at pH 5) and about 5 times more than in OSP (Soluble at pH 10) than Pb in the corresponding phases of the Gilmore sediment. These differences for the elutriate tests, however, were considerably less (Table X).

4. Manganese (Mn)

Manganese released from sediments in static column tests was not monitored. Release of trace metals in these tests was generally low: therefore, determination of their concentrations by flame AA spectrophotometry required preconcentration by solvent extraction. Trace metals Cu, Fe, Pb and Zn can be simultaneously extracted but a separate extraction run for Mn is required because of the poor stability of its chelate complexes (McQuaker, 1976). To save time Mn was omitted from these tests. The time saved was used to extend the scope of exchange studies for Cu, Fe, Pb and Zn.

The results for Fe from the static column studies may provide some insights into Mn behavior under similar

conditions. However, in view of the literature discussed by Hoffmann and Eisenreich (1981), one must use caution in projecting results obtained for one of these elements to the other. Although reactions affecting the exchange of Fe and Mn from sediments to water are similar in nature, the variations arise from differences in kinetics of the reactions and relative stabilities of the reaction products.

In elutriate tests Mn was released from both sediments and under oxic and anoxic conditions. The extent of release was independent of redox conditions but increased with salinity and became asymptotic above 4 ^{o}/oo. Also, release was slightly greater from the coarse, low organic sediment. The difference in release of Mn from the two sediments cannot be explained by the geochemical variations between the sediments. Manganese in all readily available phases such as IW, EP, ERP etc. is lower in the low organic sediment (Table X). Although total Mn is slightly higher in low organic sediment the difference does not seem to be significant. The greater release from the low organic sediment may be due to its coarser particle size and lower organic content.

Similar findings for Mn release have been made elsewhere. Chen et al. (1976) studied the release of Mn from sediments on suspension in seawater. The results for a one-half hour suspension time indicate that Mn release was independent of redox conditions and a sandy type sediment released more

Mn than a clayey type sediment. Lee et al. (1975),in a study to assess the Elutriate Test for predicting release of trace metals during dredging of contaminated sediments,noted that release of Mn depended upon sediment type among other factors but was independent of the total Mn levels in the sediments. Desorption of Mn from sediments on suspension in saltwater has also been investigated by many others (Johnson et al., 1967; Picer et al., 1973; Wagemann, 1977), but these authors did not use the standard elutriate procedure. Results of Picer et al. (1973) and Evans et al. (1977) are particularly relevant to this study. Picer et al. (1973) noted that Mn was released from limestone and aquatic sediments on suspension in water as salinity was increased from 0 - 18 $^{o}/oo$; above 18 $^{o}/oo$ the distribution coefficient of the metal between the solid and aqueous phases remained constant. Evans et al. (1977) observed a similar dependence on salinity in Newport River Estuary, North Carolina; maximum levels of dissolved Mn occurred between 4 and 14 $^{o}/oo$ salinity.

In this study, the levels of Mn in solution were much higher than for other trace metals with the exception of Fe under anoxic and low pH conditions. A recent review of the literature on potential release of contaminants from sediments during dredging and dredge disposal operations concluded that Mn as well as ammonia are the most readily released pollutants (Lee and Mariani, 1977). Lee and Mariani also measured high release of Mn in elutriate tests

on dredge materials. For a sediment to water ratio of 5:1, a maximum Mn concentration of 6 mg/l was measured.

In variable pH elutriate tests a large Mn release was observed at pH 5 as was the case for Fe. Again this was attributable to solution of Mn oxides which usually regulate solubility of Mn in oxic aquatic systems. Substantial amounts of Mn and Fe were leached with organic acids (pH 2, 4, 6) from rocks (Brockamp, 1976). At pH 5 a slightly greater release from the low organic sediment cannot be explained by geochemical differences; therefore it has to be attributed to differences in physical characteristics of the sediments.

Unlike other trace metals, minimum Mn release was measured at high pH (10). This indicates that associations of Mn with humic-like substances are weaker than for other trace metals. This is not surprising since the geochemical distribution of Mn (Table X) shows that very little Mn is bound to the OSP phase of the sediments. Also, data from Schnitzer (1969) and Irving and Williams (1948) presented by Jones (1978) show that the stability of the Mn^{2+} - Fulvic acid complex ranked 11th among a dozen different metallic ion-fulvic acid complexes. The logarithms of the stability constants of the fulvic acid-metal complexes of special interest in relation to this study are: $Fe^{3+} = 9.40$, $Cu^{2+} = 8.69$, $Pb^{2+} = 6.13$, $Fe^{2+} = 5.77$, $Mn^{2+} = 3.78$, $Zn^{2+} = 2.34$, all at pH = 5.0. A number of other authors

also report poor association of Mn with organics (Abdullah and Royale, 1972; Krom and Sholkovitz, 1978; Moore et al., 1979). Another, probably more likely, reason for the low release of Mn at high pH (10) is the oxidation of any Mn(II) to (highly insoluble) Mn(IV). The rate of oxidation of Mn(II) is highly dependent on concentration of hydroxide ion (Stumm and Morgan, 1971).

5. Zinc (Zn)

Like Pb, dissolved Zn levels in static freshwater oxic and anoxic systems rapidly dropped to equilibrium concentrations less than 10 μg/l. Durum et al.(1971) also reported Zn concentrations below 10 μg/l in some U.S. rivers. Chemical thermodynamic calculations of Hem(1972), however, indicated considerably higher levels of Zn. For example, in pure water at pH 8 the calculated Zn concentration was 400 μg/l and in the presence of carbonate species (440 mg/l as CO_2) the concentration was lowered to 25 μg/l. The presence of silicate ions was shown to further limit the concentration of Zn by 1 to 2 orders of magnitude by formation of sparingly soluble Zn_2SiO_4 (willemite). At naturally occurring silicate concentrations of about 6 mg/l, Zn concentrations of less than 40 μg/l may be attained. Co-precipitation of Zn with silica has been further investigated by Willey (1977). Hem (1972) attributed low (undersaturated) measured concentrations of Zn and Cd in rivers to removal of metals from solution by such processes as adsorption. Means et al. (1978) presented

information which shows that oxides of Mn, Fe and organics may remove trace metals from solution. O'Connor and Renn (1964) showed that the extent of adsorption of Zn may depend upon pH and the concentration of suspended sediments in water. Freshwater sediments are believed to be effective scavengers of trace metals (Iskander and Keeney, 1974; Dreher et al., 1977; Christensen and Chien, 1981).

Zinc adsorbed under freshwater conditions may be desorbed under saline conditions. After the first salinity adjustment (14.5 $^o/oo$) in oxic static column and under both oxic and anoxic conditions in elutriate tests, Zn was released into solution. Similar desorption of trace metals have been observed in a number of other studies (Bradford, 1972; Troup and Bricker, 1975; Thomas and Grill, 1977; Kharkar et al., 1968; Grieve and Fletcher, 1977). Freshwater sediments entering a saline regime as in an estuary are exposed to cations such as Na^+, Ca^{2+} and Mg^{2+} and anions Cl^- and OH^- in concentrations a thousand times or more those in the freshwaters. Consequently, equilibrium between the dissolved and adsorbed fractions of trace metals is upset and to attain a new equilibrium, Ca^{2+} and Mg^{2+} may replace trace metals in sediments. Freshly dislodged metal ions may form coordinate complexes with abundant anions such as chlorides and hydroxides (Stumm and Morgan, 1970). MCl_3^- and MCl_4^{2-} are the dominant chloride complexes at chloride concentrations of greater than 3500 ppm (Hahne and Kroontje,

1973); however, at the neutral and slightly alkaline pH of a mixture of freshwater and seawater, $M(OH)^+$ could also be important complexes because they generally have higher formation constants than the chloride complexes (Long and Angino, 1977). Rohatgi and Chen (1975) also observed the release of 60 percent of the Zn from Los Angeles River suspended sediments after reaching equilibrium in a 2:1 seawater-riverwater mixture. In another study at a higher dilution (10:1) the percent release was considerably lower, 26 percent (Chen and Hendricks, 1974). These studies confirm the importance of desorption processes and chloride complex formation in regulating the solubility of some heavy metals under brackish and marine water conditions.

In the anoxic static columns, as in the case of Pb, Zn was not released into solution under different salinity regimes. Identical results were obtained by Lu and Chen (1977); under anoxic conditions Zn concentrations remained in the sub ppb range at the sediment-seawater interface during a 30 day period for all three sediment types (silty-clay, sandy-silt, silty-sand). The redox conditions in the water column were the controlling factors for release and uptake of Zn. Under reducing conditions sulphide precipitates regulate the release of most heavy metals from sediments (Bella, 1972; Holmes et al., 1974; Engler and Patrick, 1975; Morel et al., 1975). Pohland et al. (1981) recommend that landfill leachates should be pumped back into anoxic layers

of landfill to remove trace metals as sulphide precipitates.
The relatively high concentration of Zn in the OSP phase of
the sediments reflects the deposition of Zn as sulphide under
natural conditions.

The anoxic conditions in elutriate tests failed
to prevent release of Zn as occurred under static conditions
due to insufficient time available for generation of reduced
sulphide species. The available supply of sulphides from
the IW phase appears to have been preferentially precipitated
with Cu and Pb which have lower sulphide solubility products
of 8.5×10^{-45} and 3.4×10^{-28} as compared to 1.2×10^{-23}
for Zn (CRC, 1971).

In the variable pH systems, high concentrations
of Zn were released from the sediments at pH 5 and 10. As
previously discussed, geochemical fractions EP and ERP are
highly unstable under low pH conditions and hence are easily
mobilized into solution under acidic conditions. Solubility
curves presented by Hem (1972) show that at pH 5 in the
absence of controls, Zn concentration may reach levels $>$
1000 mg/l. The presence of various ligands, as is often
the case in natural systems, may limit the concentrations
to a considerable extent. For example, in the presence of
10^{-2}M carbonic species Zn solubility is reduced to 650 mg/l.
The maximum measured concentration was 3.0 mg/l indicating
that release was limited by coordinate complexation with
various inorganic ligands as discussed above.

Despite these controls, the measured concentration of Zn was still very high as compared to the commonly measured values in natural waters (Hem, 1972).

High release of Zn at pH 5 was also measured by Patrick et al. (1977). Data presented by these authors showed that Mobile Bay sediments incubated at three pH values (5.0, 6.5 and 8.0) and four redox potentials (-150, +50, +250, +500 mV) released maximum Zn concentrations at pH 5 and at redox potential of +500 mV. This confirms the results of the present study in which oxic conditions at a pH of 5 had the highest release.

As for Cu, Pb and Fe, more Zn was measured in solution at pH 10 than at the uncontrolled neutral pH(near 7). The geochemical distribution of Zn in the sediments (Tables IX and X) shows that substantial amounts of the metal were bound in the OSP phase. According to the previous discussions on fulvic acid-metal stability constants of the last section (for Mn), Zn is expected to poorly associate with the organics in the sediments. However, the sediment organics are composed of a complex group of substances called humic substances,and fulvic acids constitute only one component of this group of substances. Therefore, Zn association with the OSP phase ,

as indicated by geochemical fractionation, is possible

through bonding to certain organic compounds other than

fulvic acids. Sediment organics (humic substances) are

known to preferentially dissolve at alkaline pH values

(Cooper and Harris, 1974). Therefore, it is likely that the

measured high solubility of Zn at pH 10 was due to dissolution

of the sediment associated organic complexes of the metal.

Shapiro (1964) noted that yellow organic acids solubilized

Zn at alkaline pH values where it should precipitate.

Some of the high solubility of Zn at pH 10 can be

attributed to its amphoteric nature. According to Hahne and

Kroontje (1973) Zn, due to its amphoteric nature, can form

soluble hydroxide complexes in alkaline waters. Model

calculations by the authors indicated at pH 10, $Zn(OH)_2$

(neglecting water molecules) has an intrinsic solubility

(molecular solubility) of 160 mg/l. However, the solubility

curves of Hem (1972) do not support this concept because the

maximum solubility of Zn as indicated by the curves for pH 10

is only 6.5 μg/l. Therefore, it is not clear to what extent

the amphoteric nature of Zn could have contributed to the

measured high solubility of the metal at pH 10.

Both at pH 5 and pH 10 release of Zn was much

greater from the high organic sediment. These differences

can be explained by geochemical distribution of Zn in the

relevant phases of the two sediments. In static tests the EP

and ERP phases, which readily dissolve under acidic conditions,

had a wide difference in Zn concentrations between the two

sediments. The sum of Zn concentrations in these two phases

in the high organic sediment was almost 10 times greater

than the sum for the low organic sediment (Tables IX and X).

In elutriate tests the sum of Zn levels in EP and ERP phases

in the high organic sediment was approximately 3.5 times the

sum for the low organic sediment. Therefore, the higher

release of Zn at pH 5 from the high organic sediment was due

to greater availability of the metal from the high organic

sediment. Similarly, for the pH 10 tests it is likely that

the greater release of Zn from the high organic sediment was

due to there being more Zn in the OSP phase of the high organic

sediment.

C.   Particulate Trace Metal Exchange (pH Effects)

1.   pH 5

Particulate trace metal levels generally reflected

the turbidity levels thus indicating that high particulate

trace metal levels were either due to resuspension of bottom

sediments or due to precipitation of metals from solution.

The initial high concentration of particulate trace metals were

due to re-suspension of sediments during the setup of the col-

umns. The later increase was related to failure of pH (5)

acetate buffer, probably due to microbial breakdown of acetate

ion. In the high organic system the failure set in earlier

because the column was resued after the low organic sediment run.

Despite a thorough clean up, bacterial contamination might have

remained, especially through the fritted glass aeration tube.

As the pH rose due to failure of the acetate buffer, Cu and Pb were substantially removed from solution and release of Fe, and Zn appears to have been inhibited. Smith (1973) has shown that metal solutions may be unstable even at pH values as low as 2. Sediments may readsorb extracted trace metals under acidic conditions; Cu and Pb adsorption has been shown to strongly depend upon pH changes (Rendell et al., 1980). According to James and MacNaughton (1977), adsorption of metal ions occurs rapidly over a narrow pH range which is characteristic of the metal ions and their complexes. In the present study a slight increase in pH (4.9→5.1) appeared to have created conditions favourable for readsorption of Cu and Pb. Iron adsorption starts at pH 5.3 and Zn seems to be least affected within the pH range of the experiments.

The loss of Cu and Pb from solution was not completely reflected by a parallel increase in the suspended particulate trace metal concentrations. This can be explained by deposition of trace metals in association with the settling particulates. Coincident with the buffer failure (by bacterial action on acetate ion), rusty colored particulates formed in the water column and some settled to the sediment layer. The bacteria associated with the settling particles probably provided an additional mechanism for Cu and Pb removal through adsorption on cell walls.

Particulate trace metal level trends for both
sediments were similar except that in the high organic
sediment, the increase due to buffer failure occurred
earlier in the run.

2. pH 7

In the pH 7 microcosms, particulate trace metal
levels were high initially due to resuspension of sediments
during set up of columns. As the sediments deposited,
particulate trace metal levels remained low with the exception
of some increases which may be attributed to resuspension of
sediments or to analytical contamination. Particulate levels
for the high organic sediment were higher because it contained
higher levels of the metals.

3. pH 10

Particulate trace metal trends at pH 10 were
similar to those of the pH 7 experiments with two important
differences. First, particulate trace metal levels dropped
more slowly, probably because the particulates were stabilized
by the organics released under alkaline conditions. Secondly,
trace metal levels were regulated by trace metal-organic
matter associations. For example, Fe and Pb are known to
strongly bind to organic humic matter; hence particulate
levels for these metals were much higher than those for Zn.
Also OSP levels of the metals in the sediments seem to be
reflected in particulate trace metals. Results show that Cu

preferentially binds to the dissolved fraction of organic humus.

III. TRACE METAL EXCHANGE AT THE SEDIMENT-INVERTEBRATE
      INTERFACE

The concentrations of all trace metals were higher in the high organic sediment. Copper, Pb and Zn associated with the OSP phase in the high organic sediment were approximately as high as the total metal levels in the low organic sediment. Greater association with the OSP phase did not result in greater accumulation of trace metals in the organisms associated with the high organic sediment.

Copper in the high organic sediment was almost three times the level found in the low organic sediment with two thirds of it bound to the OSP phase. However, chironomids accumulated higher levels of Cu from the low organic sediment and there was very little difference in accumulation of Cu by amphipods or oligochaetes in the two sediments. Therefore, OSP-bound Cu does not appear readily available to these invertebrates. Luoma and Jenne (1975a) found that radioactive cadmium, ^{109}Cd, was not available to clams when it was adsorbed to organic detritus or Fe oxide coated with organics. Similarly, Phelps (1979) observed that the Cd isotope bound to albumen was not taken up by the soft shell clam, Mya arenaria , whereas the isotope adsorbed to bentonite clay was readily absorbed. The low bioavailability of albumen-held Cd was attributed to strong bonding between the

metal and the substrate. Bryan and Hummerstone (1977) in a field survey noted that Ag in sulphide form from mining sources was not available to _Scrobicularia plana_, an estuarine bivalve mollusc. Although the similarity of behavior of Cd and Ag to Cu as indicated in these studies may be only coincidental, it is obvious that the geochemical form of trace metals in sediments may determine accumulation. Hall and Bindra (1979) in a field study found that Cu in oligochaetes was related to concentrations in EP, ERP and OSP phases. In addition, Cu concentrations in the organisms depended upon the percentage of coarse sand (0.5 - 1 mm) in the sediments. A high percentage of silt and clay depressed Cu levels in chironomids (Table 1).Similarly, in the present laboratory study, particle size seems to have played an important role. Luoma and Jenne (1976) also found no correlation between trace metal levels in bivalves and metal concentrations in the acid extractable and easily reducible fractions of the sediments. Uptake rate of sediment bound metals by invertebrates is also species specific. Ray et al. (1981) studied the uptake of Cu, Pb and Zn from two contaminated sediments by three invertebrate species. The invertebrates were exposed to the sediments for 30 day period and metal concentrations in the organisms were measured several times during the 30 day period. _Crangon septemspinosa_ and _Macoma balthica_ accumulated Cu from both sediments but in the third specie, _Nereis virens_, Cu levels at the end of 30 day period dropped slightly below the initial levels.

The Fe levels were higher in most organisms kept in the low organic sediment even though it had a slightly lower Fe concentration. However, there was four times as much exchangeable (EP) Fe in the low organic sediment which appears to be biologically available. The higher level of dissolved Fe in the interstitial water (IW) of the high organic sediment did not affect accumulation indicating that direct absorption of the dissolved element was not occurring to any measurable extent. Removal of the exchangeable (EP) Fe from the sediment probably occurs by ingestion and release in the gut of the deposit feeders. Coarseness of the low organic sediment appears to be another factor favoring greater accumulation of Fe. Although this conclusion is not statistically sound (n=2) it is supported by many (n=5) field data (Table II).[2] Characteristics of adsorption sites on coarse sediments probably are such that adsorbed Fe is readily available. In the present study, although the uptake rate of Fe was high for the amphipods and chironomids, there was only a small increase in their accumulation ratio during the study period, indicating that the organism can regulate tissue Fe levels to some extent.

Higher Pb accumulation occurred in amphipods and oligochaetes the high organic sediment microcosms. The levels

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2. Similarly, elsewhere in this thesis conclusions have been drawn from results for two sediments. Replication of experiments of this study with a large number of sediment types would be difficult and very time consuming.

of Pb in the EP, ERP and OSP phases of the high organic sediment were 5 to 6 times the values in the low organic sediment, so it is difficult to relate accumulation to a single geochemical fraction. Previous research indicated that the best relation was between total Pb in the sediment and accumulation for organisms collected in the field (Hall and Bindra, 1979). Similar relationships between Pb levels in macroinvertebrates, Asellus aquaticus L. and Erpobdella octoculata (L), and total Pb levels in the sediment substrate were found in the River Irwell, U.K. (Eyres and Pugh-Thomas, 1978). Chapman et al. (1980) also observed that in the Fraser River estuary total Pb concentrations in the sediments were reflected in the oligochaetes. A laboratory uptake experiment similar to the present study, indicated that Pb accumulated by three species of marine invertebrates, over a 30 day period, was greater from a finer sediment containing higher levels of total Pb (Ray et al., 1981). Unlike the present study, the finer sediment contained lower concentration of organic carbon; however, the difference in percent organic carbon between the two sediments was small. As in the case of Cu, Pb uptake may be affected by Fe (Luoma and Bryan, 1978). Statistical analysis of field data obtained from 17 estuaries in England and France indicated that the Pb/Fe ratio in 1N hydrochloric acid extracts of surface sediments is related to the Pb levels in the estuarine bivalve Scrobicularia plana. In the present study, metals in the non-residue fractions are approximately equivalent to metals

in a 1N hydrochloric acid extract. This amounts to 2060 ppm
Pb and 5500 ppm Fe for the low organic sediment and 987 ppm
Pb and 7900 ppm Fe for the high organic sediment. Therefore,
the Pb/Fe ratios are 0.0375 and 0.1249 for the low organic and
high organic sediments respectively. This suggests that Pb in
the high organic sediment could be 3 to 4 times more available
than in the low organic sediment. However, a number of other
factors such as particle size, organic carbon and calcium
carbonate levels may also affect availability of trace metals
(Luoma and Bryan, 1978). Therefore, the Pb uptake by inverte-
brates was not in exact proportion to the Pb/Fe ratios
(Table XIV).

Manganese levels were higher in all organisms from
the microcosm containing the low organic sediment even though
this sediment contained 100 ppm less of total Mn. No specific
geochemical fraction of Mn was at a much higher level in the
low organic sediments; therefore, the physical character
(finer particle size and higher organic level) of the high
organic sediment possibly makes the element less available
when the sediment is ingested. A field survey demonstrated
a fairly good relationship between the ERP phase (Mn bound
as oxides and carbonates) and bioaccumulation ratios in
chironomids and oligochaetes (Figure 1, adapted from Bindra
and Hall, 1977). In this laboratory study such a relationship
was not observed. A number of studies (Packer et al., 1980;

Bryan and Hummerstone, 1973; Ireland, 1979) indicate that Mn levels are regulated by organisms. The fine particle size and high organic content of the high organic sediment probably also inhibited organism uptake of Mn (Table IV, data from Bindra and Hall, 1977).

Even though there was five times the level of total Zn in the high organic sediment as well as higher levels in the chemically more available phases (EP, ERP and OSP), there was a much larger change in the bioaccumulation ratio in the low organic sediment, although the actual final concentration in the organisms was very similar to both sediments. Hall and Bindra's (1979) study indicated that Zn in oligochaetes and chironomids is negatively related to Fe in the EAEP phase of the sediments. The high organic sediment contained approximately 1.5 times more EAEP Fe than the low organic sediment, therefore, availability of Zn in the high organic sediment could be suppressed by the higher Fe levels. In a laboratory study (Romeril, 1974) similar to the present one, where uptake of ^{65}Zn from sediments to two species of oysters, Crossostrea angulata and Ostrea edulus, was investigated over a six week period, it was demonstrated that Co and Fe could inhibit the biological uptake rate of Zn. The limiting effect of Fe and Co on uptake of Zn was attributed to competition for sites at the point of uptake. Luoma and Bryan (1978) in a field investigation noted that availability of Zn in aquatic

sediments to two bivalves, <u>Macoma</u> <u>balthica</u> and <u>Scrobicularia</u> <u>plana</u>, was negatively affected by the total organic carbon content of the sediments. Ray et al. (1981) observed that uptake rate of Zn and some other trace metals in sediments was related to metal levels in EDTA extract of sediments (adsorbed, precipitated and complexed phases).

In addition to the geochemical form of the trace metal, inter-elemental interactions, and the physical chemical properties of the sediment, there are other important factors which may regulate the levels of trace metals in an organism and its ability to mobilize and excrete the element from tissue. Possibly those organisms living under high trace metal stress are induced to develop a more efficient system to eliminate trace metals. Eyres and Pugh-Thomas (1978) investigated accumulation of Cu, Pb and Zn by a freshwater louse (<u>Asellus</u> <u>aquaticus</u> L.) and a leach (<u>Erpobdella</u> <u>octoculata</u> L.) , and found lower levels of Cu and Zn in organisms living under higher environmental concentrations. They suggested a possible mechanism for excretion developing at high concentrations. Bryan (1976) also reported that some species were able to excrete a higher proportion of the trace metal intake under contaminated conditions and thereby regulate the concentration in the body at a fairly normal level. Recent research (Brown, 1978) has shown that aquatic organisms living under trace metal stress can induce synthesis of a trace metal binding protein,

metallothionein, which may aid in excretion of trace metals.
It appears that some mechanism was working for the oligochaetes
in this study since concentrations of all five trace metals
decreased after one week, increased to a peak value at four
weeks and then showed a decrease during the final week of
the microcosm. Also, the fact that some organisms showed
lower levels of trace metals when incubated in the sediments
with higher trace metals in the more chemically, and possibly
biologically, available phases suggests possible induction
of some mobilization mechanism. Stickney et al. (1975),
however, believe that if trace metals reach a certain high
level, homeostatic trace metal elimination mechanisms may be
overcome.

The decrease in the Fe and Mn concentrations in
the oligochaetes after one week from the time of transfer to
microcosms appears to have occurred at least partly due to
transfer to an environment relatively less polluted with Fe
and Mn. Ladner Sidechannel sediments, from which the oligo-
chaetes were collected for microcosm studies contained twice
as much Fe as in the microcosm sediments. Similarly Mn was
higher in the Ladner Sidechannel sediments than in the micro-
cosm sediments (Table XII), but the difference was not quite
as large as for Fe. The exposure of oligochaetes to lower Fe
and Mn concentrations in the microcosms probably resulted in
loss of these metals. The much higher levels of readily avail-
able EP phase Fe and Mn in the microcosm sediments (Table X)
probably resulted in subsequent increase in the organisms.

Microbial populations in aquatic sediments may also affect uptake rates of metals by benthic invertebrates (Patrick and Loutit, 1976). Carter (1976) in a study of uptake rates ^{85}Sr and ^{137}Cs by oribatid mites collembolans from soil and litter, noted that ^{85}Sr body burdens of the mite over a 60 day period depended on the isotope levels in fungal mycelia growing on contaminated litter. Geesey (1980) investigated the distribution of bacterial populations in sediments and associated interstitial waters in two watersheds of the Lower Mainland of British Columbia. He noted that only a small fraction of the bacteria existed as free floating cells and the majority was attached to fibrous material in the sediments. Preferential ingestion of fibrous matter or exclusion could affect metal uptake rates by the invertebrates. In the present study although bacterial population dynamics were not monitored, it is possible that the observed uptake or loss of metals by the amphipods reflected the accumulation or loss of metals from the sediments by microorganisms growing on the algae introduced to the microcosms as food for the amphipods.

From this discussion it is obvious that the trace metal uptake or loss processes are quite complex and a number of factors such as trace metal geochemistry, sediment characteristics and biology of the organisms can influence the exchange rates. A large variation in the trace metal uptake rates for different time intervals of the microcosm period probably resulted from different factors gaining control of the exchange processes at different times.

Chapter 5

SUMMARY AND SIGNIFICANCE OF RESULTS AND RECOMMENDATIONS

FOR FUTURE RESEARCH

I.   SUMMARY

The results of this laboratory study encompass a wide range of trace metal interactions which have significant management implications in the aquatic environment. Mobilization of trace metals in sediments to both water and benthic invertebrates was investigated. The results of mobilization of trace metals have been discussed with reference to trace metal geochemistry in sediments and sediment characteristics such as organic matter content and particle size distribution. Experimental conditions were kept as close as practically possible to naturally occurring conditions.

Under 'normal pH'[1] and both oxic and anoxic conditions[2] through varying salinities, release of the toxic trace metals Cu and Pb from contaminated sediments was not excessive. Under the same conditions, however, a significant release of Zn was observed. Physical character of sediments (organic matter and particle size distribution) determined

1.   Between pH 6.5 and 8.
2.   For definition of 'oxic' and 'anoxic' conditions see footnote on p. 89.

the release pattern under the normal pH conditions. Under some extreme environmental conditions, however, very high concentrations of trace metals were measured. Generally, a high release of all metals was observed at low pH (5) and high pH (10). Iron and Mn were substantially released from contaminated sediments under anoxic conditions. Agitation of sediments in a saline environment resulted in a very high release of Mn under both oxic and anoxic conditions and the release was independent of salinity above 8 ^{o}/oo.

In microcosms, the concentrations of total trace metals in sediments provided an indication of the potential for exchange with benthic invertebrates. The geochemical distribution of the trace metals as well as the physical character of the sediments influenced bioavailability. However, possible development of excretion mechanisms under high trace metal stress complicates interpretation of data on exchange mechanisms.

More specific findings for exchange across the sediment-water and sediment-biota interfaces are outlined below.

A. Trace Metal Exchange at the Sediment-Water Interface

(1) Under oxic freshwater conditions in the static column tests equilibrium concentrations of the more toxic trace metals (Cu, Pb and Zn) were less than 10 μg/l, with Fe concentrations less than 100 μg/l, even with total concentra-

tions in the sediments of several hundred ppm. There was no relationship between the level of sediment contamination and exchange of trace metals into the water. Often the high organic sediment with higher levels of trace metals released less metal into solution. The high organic content, fine particle size and high Fe and Mn levels appear to have limited release of toxic trace metals.

(2) Initial set up of columns resulted in a release of dissolved trace metals which is in agreement with observations reported by others. Solution from resuspended sediment seems to be a common problem in setting up quiescent columns even though extreme care is exercised.

(3) Unlike quiescent column tests, elutriate tests do not represent equilibrium exchange conditions. Despite this, the rapid elutriate tests confirmed many of the observations made during the long term quiescent studies.

(4) In the oxic system at low salinities some Cu and Pb and higher levels of Zn were released into solution. This was apparently attributable to desorption from Fe and Mn oxides and/or formation of chloride complexes. A greater release of Cu from the high organic sediment was attributed to break down of Cu chelates under oxic conditions. Higher concentrations of Zn were released at low salinities from the low organic sediment,even though it had a lower Zn content than the high organic sediment. Apparently organic matter helps to bind Zn tightly in the sediment and inhibits

its release by desorption and complexation processes. The geochemical differences between the two sediments were not significant enough to account for variations in trace metal release.

(5) Some Fe was released from the low organic-sandy sediment at very low salinities (4 $^{o}/oo$); however, at salinities above 10 $^{o}/oo$, Fe was readily removed from solution by flocculation processes. Manganese was released from sediments to a maximum concentration over a wide salinity range (4-26 $^{o}/oo$) and the release was slightly greater from the low organic sediment. The difference in Mn release between the two sediments could not be explained by differences in geochemical distribution of the metal. Therefore, it probably can be attributed to differences in sediment particle size.

(6) Under anoxic conditions, Fe and Mn were released in relatively high concentrations. Apparently sulphide precipitation controls the solubility of Cu, Pb and Zn under reducing conditions. In the anoxic static columns, Fe release was much higher from the low organic sediment, again demonstrating the strong binding capacity of the organic matter and a greater sulphide precipitation. Sulphide precipitation in the high organic sediment was apparent from the characteristic FeS black coloration of the surface layer.

(7) Low (5) and high (10) pH resulted in a higher

release of all trace metals than occurred at neutral pH. Release at high pH was attributable to solution of organic bound metals (a component of the OSP phase) and stabilization of metal species in solution by association with humic-like substances. This mechanism of trace metal release apparently overwhelmed the precipitation mechanisms operating under alkaline conditions. For Zn, a part of the high solubility at high pH probably was due to its amphoteric nature. Trace metal release at low pH was attributable to dissolution of Fe and Mn oxides and their associated trace metals (EP (desorption) and ERP phases). However, in more calcareous sediments, solution of carbonate precipitates and their associated trace metals would also occur.

B.   Trace Metal Exchange at the Sediment-Invertebrate Interface

(1)   Opossum shrimp were most susceptible to the toxicity of the contaminated sediments; in the more contaminated high organic sediment, mortality was 100 percent within one week.

(2)   Chironomids showed the highest uptake of all trace metals over the study period. Change in bioconcentration ratio in the low organic sediment was in the range of +0.11 to +0.73 and for the high organic sediment the change was between +0.06 and +0.10. Thus for chironomids, high organic content of sediments appeared to suppress

uptake of all five trace metals.

(3) Results for oligochaetes were highly variable, thus suggesting that these organisms had a significant capacity to both mobilize and excrete trace metals from their tissues.

(4) In amphipods, accumulation of Fe and Mn appeared to have resulted from consumption of the algae Enteromorpha which was provided as food to this organism.

(5) High Cu levels in sediment, especially when associated with the OSP component, are not readily available to benthic organisms. Sediment particle size appears to have played an important role in determining degree of Cu uptake by the organisms.

(6) Iron and Mn accumulated to higher levels in invertebrates kept in low organic sediment containing lower levels of Fe and Mn. Iron in the exchangeable phase of the low organic sediment probably was responsible for higher levels in the organisms. Physical characteristics such as coarse particle size and low organic content could be other possible causes for high uptake from the low organic sediment. The physical characteristics were apparently particularly important for higher uptake of Mn from the low organic sediment, there being no large difference in the geochemical distribution of Mn in the two sediments.

(7) Amphipods and chironomids appeared to be controlling their uptake of Fe. Although the uptake rate of

this metal was high for these organisms there was only a small increase in bioaccumulation ratio, which indicates that the organisms can regulate tissue Fe levels to some extent.

(8) A greater accumulation of Pb in amphipods and oligochaetes occurred in the high organic sediment containing higher levels of Pb in EP, ERP and OSP phases. It was difficult to attribute accumulation to a single geochemical phase.

(9) Zinc levels were higher in the organisms in the low organic sediment, as was the case for Cu, Mn and Fe, even though the low organic sediment had total Zn levels one-fifth of those in the high organic sediment. The higher organic matter and Fe levels in the high organic sediment probably inhibited uptake of Zn.

II. SIGNIFICANCE OF RESULTS

A. Impact of Trace Metal Contaminated Bottom Sediments on Water Quality

Disturbance of bottom sediments (particularly in freshwater systems) even under normal pH (6.5-8) and oxic conditions may result in high concentrations of dissolved trace metals. Fortunately, the high concentration solutions of trace metals under normal pH and oxic conditions are unstable and rapidly drop to low equilibrium levels (less than 10 μg/l). Therefore, dredging of city water supply reservoirs may be permitted without endangering health of the citizens if moderately high dissolved oxygen conditions can

be maintained at the same time. When such dredging operations must be carried out under anoxic conditions,water from the reservoir must be treated for removal of Fe and Mn before distribution for drinking. Lower dissolved trace metal levels may be expected for waters underlain by organic matter-rich fine sediments as compared to waters standing above coarse, low organic sediments with similar levels of trace metal contamination.

In estuaries under normal pH and oxic conditions , concentrations of dissolved Cu and Pb in water overlying contaminated sediments would not become high enough to have an acutely toxic effect upon most aquatic life. The concentration of Zn under changing salinity conditions, however, may reach levels of some environmental concern. Special care must be exercised when dredging contaminated sediments from estuaries or harbours because agitation of sediments in saline waters results in elevated concentrations of Mn and Zn in the water column. In elutriate tests with seawater , Mn concentrations up to 2 mg/l were measured. Such high concentrations of Mn could adversely affect some forms of aquatic life.

Under the variable pH and oxic conditions a greater release of dissolved metals occurred. The highest values for all trace metals occurred at pH 5 for the high organic sediment. Dissolved levels of Cu, Fe, Pb and Zn reached values higher than 100, 10,000 , 1,000 and 1,000 μg/l

respectively in the "static" columns. Similar concentrations
of these trace metals may be expected to occur in a system
such as a lake, provided the lake sediments are similar to
those used in this study and provided there is no renewal of
the water column. These concentrations could have some adverse
effects on aquatic biota even with limited exposure. However,
these extremely acidic conditions are ordinarily not very
likely to occur. But energy shortages in the recent years
are forcing the use of coal high in sulphur and nitrogen
elements which results in emissions of large amounts of acid
gases like SO_2 and NO_2 which wash out from the atmosphere as
acid rain. To make things worse, installation of devices by
industries for recovery of acid gases has become cost
prohibitive under the adverse economic conditions. As a
result, the probability of reaching very low pH values in
lakes and soils has increased greatly. Hence the potential
of exposure of organisms and plants in the aquatic environment
and crops in the soils to trace metal contamination has
considerably increased lately. The Coastal Mountain areas
of British Columbia, Nova Scotia and the Canadian Shield of
Ontario and Quebec, where alkalinity is too low to counteract
acid rain are more sensitive areas in Canada. Accidental
acid spills may occur anywhere and thus release high levels
of toxic trace metals.

Release of high levels of trace metals from
contaminated sediments is also possible if alkaline materials
like NaOH or KOH are accidently spilled into natural waters.

Trace metal release was high both at very low (5) and very high pH (10) conditions. The potential of trace metal release at high pH (10) is greater where sediments are rich in organics. However, the potential of naturally occurring high pH conditions is relatively less severe because industrial emissions are generally acidic.

Agitation conditions such as those in laboratory elutriate tests result in the release of higher concentrations of dissolved metals than occur under quiescent conditions. Manganese under both oxic and anoxic conditions and Fe under anoxic conditions are released in concentrations well above 1 000 μg/l and could be potentially toxic. However, it requires extreme pH conditions to cause significant release of more toxic elements such as Pb and Zn. Probably the physical disturbance with resultant sediment suspension and high turbidity would have more acute toxic impacts on aquatic organisms than would the trace metal levels.

The impact of long term exposure to lower levels of dissolved toxic metals such as those observed in this study should not be overlooked. Uptake of elements such as Pb, with an extremely long biological half-life, and the accumulation of trace metals by direct adsorption or food chain concentration processes provide a mechanism whereby even low levels can prove to be detrimental if exposure times are long.

B. **Impact of Trace Metal Contaminated Sediments on**

Benthic Invertebrates

Results of this study indicate that contamination of bottom sediments can be disastrous to some benthic species like the opossum shrimp. Its survival time in the more contaminated high organic sediment was less than one week.

Some organisms like chironomids constitute a major food source for freshwater and estuarine fish and can accumulate toxic trace metals from contaminated sediment substrates. In the process, toxic elements may be mobilized directly from sediments to food chains linked to human aquatic food sources.

Salmon fingerlings, on the way to the sea, stop at river mouths where they actively feed upon amphipods. Amphipods, as indicated by the results of this study, may accumulate high levels of Fe and Mn. Although these metals are relatively less toxic , at very high tissue levels they may affect metabolism of consumer fishes. Fortunately, the demonstrated ability of amphipods to excrete toxic elements Cu, Pb and Zn may protect fisheries from becoming contaminated and unfit for human consumption.

Oligochaete worms are considered tolerant to metal pollution. The results of this study show that the tolerance probably is a result of their ability to control levels of trace metals in their tissue.

III.   RECOMMENDATIONS FOR FUTURE STUDIES

A.   Exchange at the Sediment-Water Interface

Results of this study show that both very low (5) and very high (10) pH values promote release of dissolved trace metals from sediments.   Release at intermediate pH values (6, 8 and 9) should be investigated to determine the sensitivity of release to pH changes near the neutral value.

The effect of humic substances should also be examined by adding varying amounts of these materials isolated from organic rich sediments to test columns and elutriate mixtures. At the end of these experiments test water should be analyzed for bound (complexed) and free (ionic) metal species to determine the mechanisms of release and the nature of the released metal species.

The elutriate tests have shown that release of trace metals is more sensitive to salinity changes in the 1 to 10 ^{o}/oo range.   In columns salinity was changed from zero to above 14 ^{o}/oo in one step.   Column tests should be repeated at salinities of 1, 2, 4 and 10 ^{o}/oo to determine the effects of changing salinity on metal exchange.

The effect of sediment particle size differences on trace metal release should be further investigated to confirm the results of this study.

In addition, not all combinations of various environmental factors have been used in this investigation to determine their effect on trace metal exchange.   For

example, effect of various pH conditions under anoxic conditions (low redox potentials) has not been investigated in these experiments. Therefore, it is recommended that these experiments be further extended to include additional possible environmental conditions.

Also, experiments should be carried out to study trace metal exchange at the sediment-water interface using various dilutions of wastewater containing heavy metals such as effluent from a plating shop. The experiments should simulate different pH, oxygen and salinity conditions.

Finally, since the effect of the geochemical form of trace metals in the presence of other variables could not be selectively related to exchange rates, model sediments consisting of individual geochemical phases (EP, ERP, OSP etc.) should be used to study trace metal exchange under different environmental conditions. Although such experiments would be environmentally unrealistic, the results could provide useful insights into the effect of varying geochemical form on trace metal exchange in real situations.

B.   Exchange at the Sediment-Invertebrate Interface

To develop a much better understanding of the influence of trace metal geochemistry and sediment physical properties on accumulation, a much larger range of sediments must be subjected to similar uptake studies. Two widely different sediments did not provide the range of

trace metal geochemical distribution needed. By taking a
highly contaminated sediment and making a series of dilutions
with clean sand and fine organic matter, such as peat or fine
sawdust, the influence of some individual physical factors
on accumulation could be documented. If a complete
range of trace metals in the geochemical fractions cannot be
found a possible alternative would be to spike sediments with
different forms of trace metals and be certain they partition
into the desired chemical phase prior to studying
accumulation.

Most benthic invertebrates graze on the
microorganisms associated with detritus particles. Therefore,
future trace metal accumulation research should involve
some measure of microbial activity or biomass throughout
the study period.

Since mobilization and excretion of trace metals
can complicate interpretation of accumulation results,
the measurement of metallothionein levels or other mobilization
pathways in organisms may provide an estimate of the potential
of organisms to eliminate trace metals and adapt to a
contaminated sediment environment.

Some of these recommendations would involve an
extensive microcosm system and necessitate collection and
sorting of large numbers or organisms. Therefore, it would
require a considerable investment in technical assistance.

REFERENCES

Abdullah, M.I. and Royale, L.G. (1972). Heavy metal content of some rivers and lakes in Wales. Nature 238, 329-330.

Aller, R.C. and Cochran, J.K. (1976). Th-234/U-238 disequilibrium in near-shore sediment: particle reworking and diagenetic time scale. Earth and Planetary Science Letters 29 , 37-50.

Anderson, R.V. (1977a). Concentration of cadmium, copper, and zinc in thirty-five genera of freshwater macro-invertebrates from the Fox River, Illinois, Wisconsin. Bull. Environ. Contam. Toxicol 18(3), 345-349.

Anderson, R.V. (1977b). Concentration of cadmium, copper, lead and zinc in six species of freshwater clams. Bull. Environ. Contam. Toxicol. 18(4), 492-496.

Ash, C.P.J. and Lee, D.L. (1980). Lead, cadmium, copper and iron in earthworms from roadsite sites. Environmental Pollution (Series A) 22, 59-67.

Ayling, G.M. (1974). Uptake of cadmium, zinc, copper, lead and chromium in the Pacific Oyster, Crossostrea gigas, growing in the Tamar River, Tasmania. Water Research 8, 729-738.

Babich, H., Davis, D.L. and Stotzky, G. (1980). Acid precipitation : causes and consequences, Environment 22(4), 6-13.

Baker, W.E. (1978). The role of humic acid in the transport of gold. Geochimica et Cosmochimica Acta 42, 645-649.

Banat, K., Forstner, U. and Muller, G. (1974). Experimental mobilization of metals from aquatic sediments by nitrilotriacetic acid. Chemical Geology 14, 199-207.

Barica, J., Stainton, M.P., Hamilton, A.L. (1973). Mobilization of some metals in water and animal tissue by NTA, EDTA and TPP. Water Research 7, 1791.

B.C. Research Pamphlet: Biological and chemical leaching. Contact : Mr. A. Bruynesteyn or Dr. R.O. McElroy, 3650 Wesbrook Mall, Vancouver, B.C. (phone: (604) 224-4331).

Bella, D.A. (1972). Environmental considerations for estuarine benthal systems. Water Research 6, 1409-1418.

Benninger, L.K., Lewis, D.M., Turekian, K.K. (1975). The use of natural Pb-210 as a heavy metal tracer in the river-estuarine system. In: Marine Chemistry in the Coastal Environment, T.M. Church (ed.), Am. Chem. Soc. Symp. Ser. 18, 202-211.

Berner, R.A. (1969). Migration of iron and sulfur within anaerobic sediments during early diagenesis. Am. J. Sci. 267, 19-42.

Biggins, P.D.E. and Harrison, R.M. (1980). Chemical speciation of lead compounds in street dusts. Environmental Science and Technology 14(3), 336-340.

Bindra, K.S. and Hall, K.J. (1977). Geochemical partitioning of trace metals in sediments and factors affecting bioaccumulation in benthic organisms. Report prepared for NRC, Ottawa (contract #032-1082/6073), 59 pp.

Bissonnette, P. et al. (1975). Extent of mercury and lead uptake from lake sediments by chironomids. Presented at the 15th Hanford Life sciences Symposium, Richland, Washington, 25 pp.

Bondarenko, G.P.C. (1972). Stability of soluble coordination compounds of copper with humic and fulvic acids. Geokhimiya 8 , 1012-1023. (English Translation).

Bothner, M.H., Jahnke, R.A., Peterson, M.L. and Carpenter, R. (1980). Rate of mercury loss from contaminated estuarine sediments. Geochimica et Cosmochimica Acta 44, 273-285.

Boxma, R. (1976). Mobility of iron in the estuaries of the Rhine and the Ems relevant to plant-availability problems. Plant and Soil 44, 407-422.

Boyden, C.R. (1974). Trace element content and body size in molluscs. Nature 25, 311-314.

Boyle, E.A., Edmond, J.M.E. and Sholkovitz, E.R. (1977). The mechanism of iron removal in estuaries. Geochimica et Cosmochimica Acta 41, 1313-1324.

Bradford, W.L. (1972). A study on the chemical behavior of zinc in Chesapeake Bay water using Anodic Stripping Voltametry, Chesapeake Bay Institute, John Hopkins University, Tech. Rept. 76 (1972), Ref. 72-7, 103 pp. Baltimore, Md. 21218.

Brockamp, O. (1976). Dissolution and transport of manganese by organic acids and their role in sedimentary Mn ore formation. Sedimentology 23, 579-586.

Brooks, R.R. and Rumsby, M.G. (1965). The biogeochemistry of trace element uptake by some New Zealand bivalves. Limnology and Oceanography 10, 521.

Brown, D.A. (1978). Toxicology of trace metals: Metallothionein production and carcinogenesis. Ph.D. Thesis, Faculty of Graduate Studies, University of British Columbia, Vancouver, B.C.

Bryan, G.W. (1968). Concentrations of zinc and copper in the tissues of decapod crustaceans. Jour. Mar. Biol. Assoc. U.K. 48, 303-321.

Bryan, G.W. (1971). The effects of heavy metals (other than mercury) on marine and estuarine organisms. Proceedings of the Royal Society, London (Series B) 177, 389-410.

Bryan, G.W. (1974). Adaptation of an estuarine polychaete to sediments containing high concentrations of heavy metals. In: Pollution and Physiology of Marine Organisms, F.J. Vernberg and W.B. Vernberg (eds.), Academic Press, 123-135.

Bryan, G.W. (1976). Some aspects of heavy metal tolerance in aquatic organisms. In: Pollutants in Aquatic Organisms, A.P.M. Lockwood (ed.), Cambridge University Press, London, 7-34.

Bryan, G.W. and Hummerstone, L.G. (1971). Adaptation of the polychaete Nereis diversicolor to estuarine sediments containing high concentrations of heavy metals. I. General observations and adaptation to copper. Jour. Mar. Biol. Assoc., U.K. 51 , 845-863.

Bryan, G.W. and Hummerstone, L.G. (1973). Adaptation of Polychaete Nereis diversicolor to manganese in estuarine sediments. Jour. Mar. Biol. Assoc. U.K. 53, 859-872.

Bryan, G.W. and Hummerstone, L.G. (1977). Indicators of heavy metal contamination in the Looe Estuary (Cornwall) with particular regard to silver and lead. Jour. Mar. Biol. Assoc. U.K. 57, 75-92.

Buffle, J., Greter, F.L., Haerdi, W. (1977). Measurement of complexation properties of humic and fulvic acids in natural waters with lead and copper ion-selective electrodes. Analytical Chemistry 49, 216-222.

Bunzl, K. (1979). Competitive sorption of toxic heavy metal ions in the soil by clay minerals and soil organic matter. Proceedings International Conference on Management and Control of Heavy Metals in the Environment, Imperial College, London, Sept. 1979, 450-452.

Cammen, L.M. (1980). A method for measuring ingestion rate of deposit feeders and its use with the polychaete *Nereis succinea*. *Estuaries* 3(1), 55-60.

Carter, A. (1976). Turnover and distribution of strontium-85 and cesium-137 in soil cores kept in the laboratory. Proceedings of a Symposium on Terrestrial and Aquatic Ecological Studies of the Northwest, March 26-27, 1976, Eastern Washington State College, Cheney, Washington, 73-83.

Chao, L.L. (1972). Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Science Soc. Amer. Proc.* 36, 764-768.

Chapman, P.M., Churchland, L.M., Thomson, P.A. and Michnowsky, E. (1980). Heavy metal studies in the oligochaetes. In: *Aquatic Oligochaete Biology*, R.O. Brinkhurst and D.G. Cook (eds.), Plenum Publishing Corporation, 1980, 477-501.

Chen, K.Y. and Hendricks, T. (1974). Trace metals on suspended particulates. Southern California Coastal Waters Project, *Annual Report for the Year Ended June 30, 1974*, 147-152. El Segundo, Calif.

Chen, K.Y., Gupta, S.K., Sycip, A.Z., Lu, J.C.S., Knezevic, M. and Choi, W. (1976). Research study on the effects of dispersion, settling and resedimentation on migration of chemical constituents during open-water disposal of dredged materials. Dredged Material Research Program contract report D-76-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., 221 pp.

Cheshire, M.V., Berrow, M.L., Goodman, B.A. and Mundie, C.M. (1977). Metal distribution and nature of some Cu, Mn and V complexes in humic and fulvic acid fractions of soil organic matter. *Geochimica et Cosmochimica Acta* 41, 1131-1138.

Chester, R. and Hughs, M.G. (1967). A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chemical Geology* 2, 249-262.

Christensen, E.R. and Chien, N.K. (1981). Fluxes of arsenic, lead, zinc and cadmium to Green Bay and Lake Michigan sediments. *Environmental Science and Technology* 15, 553.

Cline, J.T. and Upchurch, S.B. (1973). Mode of heavy metal migration in the upper strata of lake sediment. Proceedings of the 16th Conference on Great Lakes Research, 1973, 349-356.

Collins, B.I. (1973). The concentration control of soluble copper in a mine tailings stream. Geochimica et Cosmochimica Acta 37, 69-75.

Cooke, M., Nickless, G., Lawn, R.E. and Roberts, D.J. (1979). Biological availability of sediment-bound cadmium to the edible cockle, Cerastoderma edule. Bull. Environ. Contam. Toxicol 23, 381-386.

Coombs, T.L. and George, S.G. (1978). Mechanisms of immobilization and detoxification of metals in marine organisms. In : Physiology and Behavior of Marine Organisms, D.S. McLusky and A.J. Berry (eds.), Pergamon Press, 179-187.

Coonley, L.S. (Jr.), Baker, E.B. and Holland, H.D. (1971). Iron in the Mullica River and Great Bay, New Jersey, Chemical Geology 7, 51-63.

Cooper, B.S. and Harris, R.C. (1974). Heavy metals in organic phases of river and estuarine sediment. Marine Pollution Bulletin 5(2), 24-26.

Corbett, R.G. (1977). The effect of coal mining on ground and surface water quality, Monongalia County , West Virginia. The Science of Total Environment 8, 21.

CRC (1971). Handbook of Chemistry and Physics, R.C. Weast (ed.) Chemical Rubber Company (CRC), Cleveland, Ohio, p. B232.

Cutshall, N., Renfro, W.C., Evans, D.W. and Johnson, V.G.(1973). Zn-65 in Oregon-Washington Continental Shelf Sediments. In : Radionuclides in Ecosystems, D.J. Nelson (ed.), Proceedings of 3rd National Symposium on Radioecology, Jan. 10-12, 1971, Oakridge, Tennessee. Sponsored by U.S. Dept. of Commerce, 694-702.

Daines, R.H., Motto, H. and Chilko, D.M. (1970). Atmospheric lead. Its relationship to traffic volume and proximity to highways. Environment Science and Technology 4, 318.

Day, J.P., Fergusson, J.E. and Chee, T.M. (1979). Solubility and potential toxicity of lead in urban street dust, Bull. Environ. Contam. Toxicol. 23, 497-502.

Dean, J.M. (1974). The accumulation of ^{65}Zn and other radionuclides by tubificid worms. Hydrobiologia 45(1), 33-38.

Desai, M.V.M., Mathew, E. and Ganguly, A.K. (1972). Interaction of some metal ions with fulvic acid isolated from marine environment. Jour. Mar. Biol. Assoc. India 14(1), 391-394.

Dreher, G.B., Muchmore, C.B. and Stover, D.W. (1977). Major, minor and trace elements of bottom sediments in Lake Du Quoin, Johnston City Lake, and Little Grassy Lake in Sothern Illinois. Environmental Geology Notes No. 82, Aug. 1977, 37 pp. Illinois State Geological Survey.

Durum, W.H., Hem, J.D. and Heidel, S.C. (1971). Reconnaissance of selected minor elements in surface waters of the United States, U.S. Geological Survey Circular No. 643, 49 pp.

Edzwald, J.K., Upchurch, J.B. and O'Melia, C.R. (1974). Coagulation in estuaries. Environmental Science and Technology 8(1), 58-63.

Elderfield, H. and Hepworth, A. (1975). Diagenesis, metals and pollution in estuaries. Marine Pollution Bulletin 6, 85-87.

Elderfield, H., Thornton, I. and Webb, J.J. (1971). Heavy metals and oyster culture in Wales. Marine Pollution Bulletin 2, 44-47.

Engler, R.M. (1976). Environmental impacts of the aquatic disposal of dredged material : fact and fancy. A working Draft, Waterways Experiment Station, Vicksburg, MS., 13 pp.

Engler, R.M. and Patrick, W.H., Jr. (1975). Stability of sulfides of manganese, iron, zinc, copper and mercury in flooded and nonflooded soils. Soil Science 119(3), 217-222.

Engler, R.M., Branon, J.M., Rose, J. and Bigham, G. (1974). A practical selective extraction procedure for sediment characterization. A draft manuscript, U.S. Army Corps of Engineers, Vicksburg, Miss., 15 pp.

Enk, M.D. and Mathis, B.J.(1977). Distribution of cadmium and lead in a stream ecosystem. Hydrobiologia 52, 153-158.

Evans, D.W. and Cutshall, N.H. (1973). Effects of ocean water on the soluble-suspended distribution of Columbia River nuclides. In : Radioactive Contamination of the Marine Environment, Proceedings of a Symposium, Seattle, July 10-14, 1972. International Atomic Energy Commission, Vienna, 125-140.

Evans, D.W., Cutshall, N.H., Cross, F.A. and Wolfe, D.A.(1977). Manganese cycling in the Newport River Estuary, North Carolina. Estuarine and Coastal Marine Science 5, 71-80.

Eyres, J.P. and Pugh-Thomas, M. (1978). Heavy metal pollution of the River Irwell (Lancashire, U.K.) demonstrated by analysis of substrate materials and macroinvertebrate tissue. Environmental Pollution 16, 129-136.

Farrah, H. and Pickering, W.F. (1977). Influence of clay-solute interactions on aqueous heavy metal ion levels. Water, Air and Soil Pollution 8, 189-197.

Feick, G., Horne, R.A. and Yeaple, D. (1972). Release of mercury from contaminated freshwater sediments by the runoff of road deicing salt. Science 175, 1142-1143.

Fillos, J. and Swanson, W.R. (1974). The release rate of nutrients from river and lake sediments. Journal Water Pollution Control Federation 46, 1032-1042.

Flegal, A.R. and Martin, J.H. (1977). Contamination of biological samples by ingested sediments. Marine Pollution Bulletin 8, 90-91.

Forester, A.J. (1980). Monitoring the bioavailability of toxic metals in acid-stressed shield lakes using pelecypod molluscs (clams, mussels). In : Trace Substances in Environmental Health, Vol. XIV, D.D. Hemphill (ed.). Proceedings University of Missouri's 14th annual conference on Trace Substances in Environmental Health, June 1980, 142-147.

Forstner, V. and Wittmann, G.T.W. (1979). Metal Pollution in the Aquatic Environment, Springer Verlag, N.Y., 247-270.

Fowler, S.W. and Oregioni, B. (1976). Trace metals in mussels from the NW Mediterranean, Marine Pollution Bulletin 7, 26.

Fowler, S.W., Oregioni, B., La Rosa, J. and Renfro, W.C. (1974). Trace element concentrations in mussels of the Ligurian Sea. Report IAEA-163, International Atomic Energy Agency, Vienna, 119 pp.

Funk, W.H., Miller, R.J., Johnson, R.D., Williams, R.E., Wai, C.M., Wiese, A.C. and Mitchell, J.E. (1977). Heavy metal problem of Silver Valley, North Idaho. In : Heavy Metals in the Environment, Vol. II, T.C. Hutchinson (ed.), Proceedings International Conference, Toronto, Oct. 27-30, 1975,

Gale, N.L., Wixon, B.G., Hardie, M.G. and Jennett, J.C. (1973). Aquatic organisms and heavy metals in Missouri's new lead belt. Water Resources Bulletin 9(4), 673-688.

Galloway, J.N., Schofield, C.L., Yost, E. and Likens, G.E. (1976). Influence of acid precipitation on the water and sediment geochemistry of Adirondack Mountain lakes. Abstracts 39th annual Meeting ASLO, Savannah, 1976.

Gambrell, R.P., Khalid, R.A. and Patrick, W.H. Jr. (1980). Chemical availability of mercury, lead, and zinc in Mobile Bay sediment suspensions as affected by pH and oxidation-reduction conditions. Environmental Science and Technology 14(4), 431-436.

Geesey, G.G. (1980). The distribution of heavy metals among constituents of the Lower Fraser River sediment. An unpublished research report, Department of Microbiology and Biochemistry, University of Victoria, Victoria, B.C.

Gibbs, R.J. (1973). Mechanisms of trace metal transport in rivers. Science 180, 71-73.

Gish, C.D. and Christensen, R.E. (1973). Cadmium, nickel, lead and zinc in earthworms from roadside soil. Environmental Science and Technology 7, 1060-1062.

Gordon, D.C. (1966). The effects of the deposit feeding polychaete, Pectinaria gouldii , on the intertidal sediment of Barnstable Harbour. Limnology and Oceanography 11, 327-332.

Graham, W.F., Bender, M.L. and Klinkhammer, G.P. (1976). Manganese in Narragansett Bay. Limology and Oceanography 21, 665-673.

Gregor, C.D. (1972). Communication : Solubilization of lead in lake and reservoir sediments by NTA. Environmental Science and Technology 6, 278-279.

Greig, R.A. and Wenzloff, D.R. (1978). Metal accumulation and depuration by the American Oyster, Crassostrea virginica. Bull. Environ. Contam. Toxicol. 20, 499-504.

Grieve, D. and Fletcher, K. (1977). Interactions between zinc and suspended sediments in the Fraser River Estuary, British Columbia. Estuarine and Coastal Marine Science 5, 415-419.

Groot, A.J. de, Salomons, W. and Allersma, E. (1976). Processes affecting heavy metals in estuarine sediments. In : Estuarine Chemistry, J.D. Burton and P.S. Liss (eds.), Academic Press, 131-157.

Gupta, S.K. and Chen, K.Y. (1975). Partitioning of trace metals in selective chemical fractions of nearshore sediments. Environmental Letters 10(2), 129-158.

Gupta, G.C. and Harrison, F.L. (1980). Effect of kaolin concentration on distribution coefficient of copper. Water, Air and Soil Pollution 13, 247-250.

Gustafson, J.F. (1972). Beneficial effects of dredging turbidity. World Dredging and Marine Construction 8, 44-52.

Guthrie, R.K., Davis, E.M., Cherry, D.S. and Murray, H.E. (1979). Biomagnification of heavy metals by organisms in a marine microcosm. Bull. Environ. Contam. Toxicol. 21, 53-61.

Hahne, H.C.H. and Kroontje, W. (1973). Significance of pH and chloride concentration on behavior of heavy metal pollutants : mercury (II), cadmium (II) and lead (II). Journal of Environmental Quality 2, 444-450.

Hakanson, L. (1974). Mercury in some Swedish lake sediments. Ambio 3(1), 37-43.

Hall, K.J., Unpublished data. University of British Columbia, Westwater Research Centre, Vancouver, B.C.

Hall, K.J. and Bindra, K.S. (1979). Geochemistry of selected metals in sediments and factors affecting organism concentrations. A paper presented at the International Conference on Management and Control of Heavy Metals in the Environment, Imperial College, London, Sept. 1979.

Hall, K.J. and Yesaki, I. Unpublished data. University of British Columbia, Westwater Research Centre, Vancouver, B.C.

Hall, K.J., Yesaki, I. and Chan, J. (1976). Trace metals and chlorinated hydrocarbons in the sediments of a metropolitan watershed. Technical Report No. 10, Westwater Research Centre, University of British Columbia, Vancouver, B.C.

Hanes, R.E., Zelazny, L.W. and Blaser, R.E. (1970). Effects of deicing salts on water quality and biota; literature review and recommended research. National Highway Research Program Report No. 91, HRB, 70 pp.

Hem, J.D. (1960). Complexation of ferric iron with tannic acid. U.S. Geological Survey Water Supply Paper 1459D, 75-94.

Hem, J.D. (1972). Chemistry and occurrence of cadmium and zinc in surface water and groundwater. Water Resources Research 8(3), 661-679.

Hem, J.D. and Cropper, W.H. (1959). Survey of ferrous-ferric chemical equilibria and redox potentials. U.S. Geological Survey Water Supply Paper 1459-A, 31 pp.

Hem, J.D. and Durum, W.H. (1973). Solubility and occurrence of lead in surface water. Journal American Water and Waste Association 65, 562-568.

Henderson, R.W., Andrews, D. and Lightsey, G.R. (1979). Leaching of lead from ceramics. Bull. Environ. Contam. Toxicol. 21, 102-104.

Hoffmann, M.R. and Eisenreich, J.J. (1981). Development of a computer generated equilibrium model for the variation of iron and manganese in the hypolimnion of Lake Mendota. Environmental Science and Technology 15(3), 339-344.

Holmes, C.W., Slade, E.A. and McLerran, C.J. (1974). Migration and redistribution of zinc and cadmium in marine estuarine system. Environmental Science and Technology 8(3), 255-259.

Holmgren, G.S. (1967). A rapid citrate-dithonite extractable iron procedure. Soil Science Soc. Amer. Proc. 31, 210-211.

Hutchinson, G.E. (1957). A Treatise on Limnology, Vol. 1, Wiley and Sons, New York, 1015 pp.

Icely, J.D. and Nott, J.A. (1980). Accumulation of copper within the "Hepatopancreatic" Caeca of Corophium volutator (Crustacea; Amphipoda). Marine Biology 57, 193-199.

Ireland, M.P. (1975). Metal content of Dendrobaena rubida (oligochaete) in a base metal mining area. Oikas 26, 74-79.

Ireland, M.P. (1979). Metal accumulation by the earthworms Lumbricus rubellus, Dendrobaena veneta and Eiseniella tetraedra in heavy metal polluted sites. Environmental Pollution 19, 201-206.

Irving, H. and Williams, R.J.P. (1948). Order of stability of metal complexes. Nature, London 162, 746-747.

Iskandar, I.K. and Keeney, D.R. (1974). Concentration of heavy metals in sediment cores from selected Wisconsin Lakes. Environmental Science and Technology 8(2),165-170.

Jackson, M.L. (1958). Soil Chemical Analysis, Prentice-Hall, Inc. Englewood Cliffs, N.J., 498 pp.

James, R.O. and MacNaughton, M.G. (1977). The adsorption of aqueous heavy metals on inorganic minerals. Geochimica et Cosmochimica Acta 41, 1549-1555.

Jenne, E.A. (1968). Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water - The significant role of hydrous Mn and Fe oxides. In : Trace Inorganics in water, ACS Adv. Chem. Ser. 73, Washington, D.C., 337-387.

Johnson, V.G. (1966). Retention of Zn-65 by Columbia River sediment. M.S. Thesis, Oregon State University, Corvallis, 56 pp.

Johnson, V., Cutshall, N. and Osterberg, C. (1967). Retention of zinc-65 by Columbia River sediment. Water Research 3(1), 99-102.

Jones, R.E. (1978). Heavy metals in the estuarine environment, Water Research Centre Coasts and Estuarine Div. (U.K.), Technical Report No. TR73, April 1978, 128 pp.

Jones, B.F. and Bowser, C.J. (1978). Factors of importance in sediment-water interaction. In: Lakes: Chemistry, Geology and Physics; A. Lermer (ed.), N.Y., 182-190.

Jones, B.F., Kennedy, V.C. and Zellweger, G.W. (1974). Comparison of observed and calculated concentrations of dissolved Al and Fe in stream water. Water Resources Research 10, 791-793.

Kee, N.S. and Bloomfield, C. (1961). The solution of some minor element oxides by decomposing plant materials. Geochimica et Cosmochimica Acta 24, 206-225.

Khalid, R.A., Patrick, W.H. Jr. and Gambrell, R.P. (1978).
Effect of dissolved oxygen on chemical transformations of
heavy metals, phosphorus and nitrogen in an estuarine
sediment. Estuarine and Coastal Marine Science 6, 21-35.

Kharkar, D.P., Turekian, K.K. and Bertine, K.K. (1968).
Stream supply of dissolved silver, molybdenum antimony,
selenium, chromium, cobalt, rubidium and cesium to the
oceans. Geochimica et Cosmochimica Acta 32, 285-298.

Kitano, Y., Skata, M. and Matsumoto, E. (1980). Partitioning
of heavy metals into mineral and organic fractions in a
sediment core from Tokyo Bay. Geochimica et Cosmochimica
Acta 44, 1279-1285.

Koenings, J.P. (1976). In situ experiments on the dissolved
and colloidal state of iron in an acid bog lake. Limonology
and Oceanography 21, 674-683.

Krauskopf, K.B. (1967). Introduction to Geochemistry, McGraw-
Hill, New York, N.Y., 706 pp.

Krom, M.D. and Sholkovitz, E.R. (1978). On the association
of iron and manganese with organic matter in anoxic marine
waters. Geochimica et Cosmochimica Acta 42, 607-611.

Kunkel, R. and Manahan, S.E. (1973). Atomic absorption
analysis of strong heavy metal chelating agents in water
and waste water. Analytical Chemistry 45(8), 1465-1468.

Larsen, P.F. (1979). The distribution of heavy metals in
the hard clam, Mercenaria mercenaria in the Lower Chesapeake
Bay Region. Estuaries 2, p.1.

Laube, V., Ramamoorthy, S. and Kushner, D.J. (1979).
Mobilization and accumulation of sediment bound heavy metals
by algae. Bull. Environ. Contam. Toxicol. 21, 763-770.

Lee, G.F. and Mariani, G.M. (1977). Evaluation of the
significance of waterway sediment-associated contaminants
on water quality at the dredged material disposal site.
Reprint from the special technical publication 634, ASTM,
1916 Race St., Philadelphia, Pa.

Lee, G.F., Piwoni, M.D., Lopez, J.M., Mariani, G.M.,
Richardson, J.S., Homer, D.H. and Saleh, F. (1975).
Research study for the development of dredged material
disposal criteria. Dredge Material Research Program
contract report D-75-4, U.S. Army Engineer Waterways
Experiment Station, Vicksburg, Miss. 337 pp.

Lee, G.F. and Plumb, R.H. (1974). Literature review on research study for the development of dredged material disposal criteria. Contract Report D-74-1, U.S. Army Waterways Experiment Station, C.E. Vicksburg, Miss.

Leeper, G.W. (1972). Reactions of heavy metals with soils with special regard to their application in sewage wastes. A report prepared for the Dept. of Army Corps of Engineers under contract No. DACW73-73-C0026.

LeLand, H.V., Luoma, S.N., Elder, J.F. and Wilkes, D.J. (1978). Heavy metals and related trace metals - A literature review. Journal Water Pollution Control Federation 50, 1469-1514.

Leudtke, N.A. and Bender, M.L. (1979). Tracer study of sediment-water interactions in Estuaries. Estuarine and Coastal Marine Science 9, 643-651.

Lewis, D.M. (1977). The use of Pb-210 as a heavy metal tracer in the Susquehanna River System. Geochimica et Cosmochimica Acta 41, 1557-1564.

Lindberg, S.E. and Harriss (1977). Release of mercury and organics from resuspended near-shore sediments. Journal Water Pollution Control Federation 49(12), 2479-2487.

Long, D.T. and Angino, E.E. (1977). Chemical speciation of Cd, Cu, Pb and Zn in mixed freshwater seawater and brine solutions. Geochimica et Cosmochimica Acta 41, 1183-1191.

Lopez, J.M. and Lee, G.F. (1977). Environmental chemistry of copper in Torch Lake, Michigan. Water, Air and Soil Pollution 8, 373-385.

Loutit, M.W., Loutit, J.S. and Brooks, R.R. (1967). Differences in molybdenum uptake by microorganisms from the rhizosphere of Raphanus sativus L., grown in two soils of similar origin. Plant Soil 27, 335-346.

Loutit, M.W., Patrick, F.M. and Malthus, R.S. (1973). The role of metal concentrating bacteria in a food chain in a river receiving effluent. Proceedings Univ. Otago Medical School 51, 37-38.

Lu, J.C.S. and Chen, K.Y. (1977). Migration of chemical constituents in sediment-water interfaces. In: Chemistry of Marine Sediments, T.F. Yen (ed.), Ann Arbor Publishers Inc., Chapter 12, 181-222.

Lu, P., Metcalf, R.L., Furman, R., Vogel, R. and Hassett, J. (1975). Model ecosystem studies of lead and cadmium and of urban sewage sludge containing these elements. Jour. Envirn. Qual. 4(4), 505-509.

Luoma, S.N. and Bryan, G.W. (no date). A statistical assessment of the control on concentrations of Ag, Cd, Co and Cu in bivalves (Scrobicularia plana) and polychaetaes (Nereis diversicolor) from 18 estuaries. A manuscript, 32 pp.

Luoma, S.N. and Bryan, G.W. (1978). Factors contrlling the availability of sediment-bound lead to the estuarine bivalve Scrobicularia plana. Jour. Mar. Biol. Assoc. U.K. 58, 793-802.

Luoma, S.N. and Bryan, G.W. (1979). Trace metal bioavailability: modeling chemical and biological interactions of sediment-bound zinc. In: Chemical Modeling in Aqueous Systems , E.A. Jenne (ed.), A.C.S. Symp. Series 93 American Chemical Society, Washington, D.C., 577-609.

Luoma, S.N. and Jenne, E.A. (1975a). Factors affecting the availability of sediment bound Cd to the estuarine deposit-feeding clam, Macoma balthica. Fourth National Symposium on Radioecology, Corvallis, Oregon, May 1975.

Luoma , S.N. and Jenne, E.A. (1975b). The availability of sediment-bound cobalt, silver and zinc to a deposit feeding clam, Macoma balthica. Fourth National Symposium on Radioecology, Corvallis, Oregon, May 1975.

Luoma, S.N. and Jenne, E.A. (1976). Estimating bioavailability of sediment bound trace metals with chemical extractants. Trace Substances in Environment health X, 343-351. University of Missouri (D.O. Hemphill, editor).

MacPherson, L.B., Sinclair, N.R. and Hayes, F.R. (1958). Lake water and sediment-III. The effect of pH on the partition of inorganic phosphate between water and oxidized mud or ash. Limnology and Oceanography 3, 318.

Malo, B.A. (1977). Partial extraction of metals from aquatic sediments. Environmental Science and Technology 11, 277-282.

Mann, A.W. and Deutscher, R.L. (1977). Solution geochemistry of copper in water containing carbonate, sulfate and chloride ions. Chemical Geology 19, 253-265.

Mathis, B.J. and Cummings, T.F. (1973). Selected metals in the sediments, water and biota in the Illinois River. Journal Water Pollution Control Federation 45(7), 1573-1583.

McKenzie, R.M. (1972). The sorption of some heavy metals by the lower oxides of manganese. Geoderma 8, 29-35.

McNurney, J.M., Larimore, R.W. and Wetzel, M.J. (1975). Distribution of lead in the sediments and fauna of a small mid western stream. In: Biological Implications of Metals in the Environment, Proceedings of 15th Annual Hanford Life Sciences Symposium at Richland, Washington, Sept. 29 to Oct. 1, 1975.

McQuaker, N.R. (1976). A Laboratory Manual for the Chemical Analysis of Waters, Wastewaters, Sediments and Biological Tissues, Water Resource Service Laboratory, Vancouver, Dept. of Environment, Province of British Columbia.

Means, J.L., Crerar, D.A., Borcsik, M.P. and Duguid, J.O. (1978). Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments. Geochimica et Cosmochimica Acta 42, 1763-1773.

Menon, M.P., Ghuman, G.S., and Emeh, C.O. (1979). Trace element release from estuarine sediments of South Mosquito Lagoon near Kennedy Space Centre. Water, Air and Soil Pollution 12, 295-306.

Moore, R.M., Burton, J.D., Williams, P.J. leB. and Young, M.L. (1979). The behavior of dissolved organic material, iron and manganese in estuarine mixing . Geochimica et Cosmochimica Acta 43, 919-926.

Morel, F.M.M., Westall, J.C., O'Melia, C.R. and Morgan, J.J. (1975). Fate of trace metals in Los Angeles County wastewater discharge. Environmental Science and Technology 9(8), 756-761.

Morgan, J.J. and Stumm, W. (1964). The role of multivalent metal oxides in limnological transformations, as examplified by iron and manganese. 2nd International Conference Water Pollution Research 6, 1-16.

Mortimer, C.H. (1941). The exchange of dissolved substances between mud and water in lakes-Part I and II. Jour. Ecol. 29, 280-329.

Mortimer, C.H. (1942). The exchange of dissolved substances between mud and water in lakes - Parts III and IV. Jour. Ecol. 30, 147-201.

Mortimer, C.H.(1971). Chemical exchanges between sediments and water in the Great Lakes - speculations on probable regulatory mechanisms. Limnology and Oceanography 16(2), 387-404.

Motto, H.L., Daines, R.H., Chilko, D.M. and Moto, E.K. (1970). Lead in soils and plants: its relation to traffic volume and proximity to highways. Environmental Science and Technology 4, 231.

Murphy, C.B. (1981). Bioaccumulation and toxicity of heavy metals and related trace elements. Journal Water Pollution Control Federation 53(6), 993-999.

Namminga, H. and Wilhm, J. (1977). Heavy metals in water, sediments and chironomids. Journal Water Pollution Control Federation 49, 1725-1731.

Naumov, V.N., Pachadzhanov, D.N. and Burichenko, T.I. (1972). Copper, bismuth, silver, lead and zinc in waters of supergene zone. Geochem. Int. 9, 129-134.

Nehring, R.B., Nisson, R. and Minasian, G. (1979). Reliability of aquatic insects versus water samples as measures of aquatic lead pollution. Bull. Environ. Contam. Toxicol. 22, 103-108.

Oakley, S.M., Delphey, C.E., Williamson, K.J. and Nelson, P.O. (1980). Kinetics of trace metal partitioning in model anoxic marine sediments. Water Research 14, 1067-1072.

O'Connor, J.T. and Kester, D.R. (1975). Adsorption of copper and cobalt from freshwater and marine systems. Geochimica et Cosmochimica Acta 39, 1531-1543.

O'Connor, J.T. and Renn, C.E. (1964). Soluble-adsorbed zinc equilibrium in natural waters. Jour. American Water Works Association 56, 1055-1081.

Okutani, K. and Okaichi, T. (1971). Heavy metals, chemical characteristics, and bacterial populations in the bottom sediments of Hiuchinada. Tech. Bull. Fac. Agric. Kagawa Univ. 23, 137-148.

Packer, D.M., Ireland, M.P. and Wootton, R.J. (1980). Cadmium, copper, lead, zinc and manganese in the polychaetae Arenicola marina from sediments around the coast of Wales. Environmental Pollution (Series A) 22, 309-321.

Patel, B., Patel, S. and Pawar, S. (1978). Desorption of radioactivity form nearshore sediment. Estaurine and Coastal Marine Science 7, 49-58.

Patrick, F.M. and Loutit, M. (1976). Passage of metals in effluents, through bacteria to higher organisms. Water Research 10, 333-335.

Patrick, W.H. Jr. and Mikkelsen, D.L. (1971). Plant nutrient behavior in flooded soil. In: Fertilizer Technology and Use, 2nd edition, Soil Science Society of America, Inc., Madison, Wisconsin, 187-215.

Patrick, W.H. Jr., Gotoh, S. and Williams, B.G. (1973). Strengite dissolution in flooded soils and sediments. Science 179, 564-565.

Patrick, W.H.Jr., Gambrell, R.P. and Khalid, R.A. (1977). Physicochemical factors regulating solubility and bioavailability of toxic heavy metals in contaminated dredged sediment. Journal Environ. Sci. Health A12(19), 475-492.

Payne, K. and Pickering, W.F. (1975). Influence of clay-solute interactions on aqueous copper ion levels. Water, Air and Soil Pollution 5, 63-69.

Perdue, E.M., Beck, K.C. and Reuter, J.H. (1976). Organic complexes of iron and aluminum in natural waters. Nature 260(5550), 418-420.

Phelps, H.L. (1979). Cadmium sorption in estuarine mud-type sediment and the accumulation of cadmium in the soft shell clam, Mya arenaria Estuaries 2(1), 40-44.

Picer, M., Picer, N. and Strahal, P. (1973). Fixation of manganese on quartz, limestone, dolomite and marine sediment samples. Health Physics 25, 285-300.

Pohland, F.G., Gould, J.P., Ramsey, R.E., Spiller, B.J. and Esteves, W.R. (1981). Containment of heavy metals in landfills with leachate recycle. In: Land Disposal : Municipal Solid Waste, Proceeding of Seventh Annual Research Symposium, EPA-600, 19-81-002a, March 1981, 179-194.

Poldoski, J.E. and Glass, G.E. (1977). Considerations of trace element chemistry for streams in the Minnesota-Ontario border area. In: Symp. Proc. Int. Conf. Heavy Metals in the Environment, Vol. II, T.C. Hutchinson (ed.), University of Toronto Press, p. 901.

Popham, J.D., Johnson, D.C. and D'Auria, J.M. (1980).
Mussels (Mytilus edulis) as 'point source' indicators
of trace metal pollution. Marine Pollution Bulletin 11,
261-263.

Presley, B.J., Brooks, R.R. and Kaplan, I.R. (1967).
Manganese and related elements in the interstitial water
of marine sediments. Science 158, 906-910.

Presley, B.J., Kolodny, Y., Nissenbaum, A. and Kaplan, I.R.
(1972). Early diagenesis in a reducing fjord, Sannich
Inlet, British Columbia --II. Trace element distribution
in interstitial water and sediment. Geochimica et
Cosmochimica Acta 36, 1073-1090.

Pringle, B.H., Hissong, D.E., Katz, E.L. and Mulawka, S.T.
(1968). Trace metal accumulation by estuarine mollusks.
Jour. Sanitary Engineering Div., Proc. American Soc. of
Civil Engineers 94, 455-475.

Ramamoorthy, S. and Rust, B.R. (1978). Heavy metal exchange
processes in sediment-water systems. Environmental
Geology 2(3), 165-172.

Rashid, M.A. and Leonard, J.D. (1973). Modifications in the
solubility and precipitation behavior or various metals as
a result of their interaction with sedimentary humic acid.
Chemical Geology 11, 89-97.

Rawson, J. (1963). Solution of manganese dioxide by tannic
acid. U.S. Geological Survey Prof. Paper 475-C,
C218-C219.

Ray, S., McLeese, D.W. and Metcalfe, C.D. (1979a). Heavy
metals in sediments and in invertebrates from three coastal
areas in New Brunswick, Canada, a natural bioassay.
International Council for the Exploration of the Sea.
C.M. 1979/E: 29.

Ray, S., McLeese, D.W. and Pezzack, D. (1979b). Chelation
and inter-elemental effects on the bioaccumulation of heavy
metals by marine invertebrates. Proceedings International
Conference on Management and Contol of Heavy Metals in the
Environment, Imperial College, London, Sept. 1979, p.35.

Ray, S. , McLeese,D.W. and Peterson, M.R. (1981).
Accumulation of copper, zinc, cadmium and lead from two
contaminated sediments by three marine invertebrates- a
laboratory study. Bull. Environ. Contam. Toxicol. 26,315-322.

Rendell, P.S., Batley, G.E. and Cameron, A.J. (1980). Adsorption as a control of metal concentrations in sediment extracts. Environmental Science and Technology 14(3), 314-318.

Reuter, J.H. and Perdue, E.M. (1977). Importance of heavy metal-organic matter interactions in natural waters. Geochimica et Cosmochimica Acta 41, 325-334.

Revitt, D.M. and Ellis, J.B. (1980). Rain water leachates of heavy metals in road surface sediments. Water Research 14, 1403-1407.

Rhoads, D.C. (1963). Rates of sediment reworking by yoldia limatula in Buzzards Bay, Mass. and Long Island Sound. Journal of Sedimentary Petrology 33(3), 723-727.

Robbins, J.A. and Edington, D.W. (1975). Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochimica et Cosmochimica Acta 39, 285-304.

Robertson, D.E., Silker, W.B., Langford, J.C., Peterson, M.R. and Perkins, R.W. (1973). In: Radioactive Contamination of the Marine Environment, Proc. Symp., Seattle, July 10-14, 1972, sponsored by International Atomic Energy Agency, Vienna, 141-158.

Rohatgi, N. and Chen, K.Y. (1975). Transport of trace metals by suspended particulates on mixing with seawater. Journal Water Pollution Control Federation 47(9), 2298-2316.

Romeril, M.G. (1974). The uptake and distribution of ^{65}Zn in oysters. Marine Biology 9, 347-354.

Romeril, M.G. (1979). The occurrence of copper, iron and zinc in the hard shell clam, Mercenaria mercenaria, and sediments of Southampton Water. Estuarine and Coastal Marine Science 9, 423-434.

Saar, R.A. and Weber, J.H. (1980). Lead (II)-fulvic acid complexes. Conditional stability constants, solubility and implications for lead (II) mobility. Environmental Science and Technology 14(7), 877-880.

Sanchez, I. and Lee, G.F. (1973). Sorption of copper on Lake Monona sediments-effect of NTA on copper release from sediments. Water Resources Research 7, 587-593.

Sanchez, I. and Lee, G.F. (1978). Environmental chemistry of copper in Lake Monona, Wisconsin. Water Research 12, 899-903.

Schink, D.R. and Guinasso, N.L. Jr. (1977). Effects of bioturbation on sediment-seawater interaction. Marine Geology 23, 133-154.

Schnitzer, M. (1969). Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Proceedings Soil Science Society of America 33, 75-81.

Schnitzer, M. and Skinner, S.I.M. (1967). Organo-matallic interactions in soils: 7. Stability constants of lead (II)-, nickel II)-, manganese (II)-, cobalt (II)-, calcium (II)-, and magnesium (II)-fulvic acid complexes. Soil Science 103, 103-247.

Scott, W.S. (1980). Occurrence of salt and lead in snow dump sites. Water, Air and Soil Pollution 13, 187-195.

Sensi, N., Griffith, S.M., Schnitzer, M. and Townsend, M.G. (1977). Binding of ferric ion by humic materials. Geochimica et Cosmochimica Acta 41 , 969-976.

Serne, R.J. (1975). Geochemical distribution of selected trace metals in San Francisco Bay sediments. Presented at 15th Hanford Life Science Symposium, Richland , Washington, Sept. 29 to Oct. 1, 1975.

Shannon, E.E., Fowlie, P.J.A. and Rush, R.J. (1974). A study of nitrilotriacetic acid (NTA) degradation in a receiving stream. Wastewater Technology Centre LEPS Report No. EPS4-WP-74-7.

Shapiro, J. (1964). Effect of yellow organic acids on iron and other metals in water. Jour. American Water and Waste Association 64, 1062-1081.

Sholkovitz, E.R. (1976). Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochimica et Cosmochimica Acta 40, 831-845.

Smith, A.E. (1973). A study of the variation with pH of the solubility and stability of some metal ions at low concentrations in aqueous solution. Part II. Analyst 98, 209-212.

Spencer, D.W. and Brewer, P.G.(1971). Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. Journal of Geophysical Research 76(24) , 5877-5892.

Standard Methods for the Examination of Water and Wastewater, 1975. 14th edition, APHA, AWWA and WPCF.

Stevenson, F.J. and Ardakarni, M.S. (1972). Organic matter reactions involving micronutrients in soils. In: Micronutrients in Agriculture, Soil Science Society of America, Inc., Madison, Wisconsin, 79-114.

Stickney, R.R., Windom, H.L., White, D.B. and Taylor, F.E. (1975). Heavy-metal concentrations in selected Georgia Estuarine organisms with comparative food-habit data. Mineral cycling in Southeastern Ecosystems, Ga, May 1-5, 1975, Technical Information Centre, ERDA.

Stokes, P.M. and Szokalo, A.M. (1977). Sediment-water interchange of copper and nickel in experimental aquaria. Proceedings 12th Canadian Symposium on Water Pollution Research in Canada, 1977.

Stoveland, S., Lester, J.N. and Perry, R. (1980). Response to comments by A.P. Walker, W.F. Holman and R.H. Wendt. Water Research 14, 395-400.

Stumm, W. and Lee, G.F. (1960). The chemistry of aqueous iron Schweiz Z. Hydrologie 22, 295-319.

Stumm, W. and Morgan, J.J.(1970). Aquatic Chemistry, Willey Interscience, New York, N.Y., 583 pp.

Szalay, A. and Szilazi, M. (1968). Accumulation of microelements in peat humic acids and coals. In: Advances in Organic Geochemistry, P.A. Schenk (ed.), Elmsford, New York, Pergammon, p. 567.

Takeuchi, T. (1972). Distribution of mercury in the environment of Minimata Bay and the inland Ariake Sea. In: Environmental Mercury Contamination. R. Hartung and B.D. Dinman (eds.), Ann Arbor Science Publishers Inc., 79-81.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. A reprint from Analytical Chemistry 51(7), 844-851.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1980). Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). Canadian Journal of Earth Science 17, 90.

Thomas, D.J. and Grill, E.V. (1977). The effect of exchange reactions between Fraser River sediment and seawater dissolved Cu and Zn concentrations in the Strait of Georgia. Estuarine and Coastal Marine Science 5, 421-427.

Thompson, J.A.J. (1974). Copper and zinc levels in submerged mine tailings at Britannia Beach, B.C., Fish. Res. Bd. Can. Tech. Report 437, 33 pp.

Thompson, J., Turekian, K.K. and McCaffrey, R.J. (1975). The accumulation of metals in and release from sediments of Long Island Sound. In: Estuarine Research, L.E. Cronin (ed.), Academic Press , New York, 28-44.

Troup, B.N. and Bricker, O.P. (1975). Processes affecting the transport of materials from continents to oceans. In: Marine Chemistry in the Coastal Environment, T.M. Church (ed.), AM. Chem. Soc. Symp., Ser. 18, 133-151.

Turekian, K.K. (1971). Rivers, tributaries and estuaries. In: Impingement of Man on the Oceans, D.W. Hood (ed.), New York, Wiley-Interscience, 9-74.

Turekian, K.K. (1977). The fate of metals in the oceans. Geochimica et Cosmochimica Acta 41, 1139-1144.

U.S. EPA (1971). Environmental impact of highway deicing. U.S. Rnvironmental Protection Agency, Edison Water Quality Laboratory, 134 pp.

U.S. EPA (1973a). Ocean dumping criteria. Federal Register 38(94), 12872-12877.

U.S.EPA (1973b). Ocean dumping final criteria. Federal Register 38(198), 28610-28621.

Van Hook, R.I. (1974). Cadmium, lead and zinc distribution between earthworms and soils. Potential for biological accumulation. Bull. Environ. Contam. and Toxicol. 12, 509-513.

Wagemann, R., Brunskill, G.J. and Graham, B.W. (1977). Composition and reactivity of some river sediments from the MacKenzie Valley, N.W.T., Canada. Environmental Geology 1, 349-358.

Wakeman, T.H. (1977). Release of trace constituents from sediments resuspended during dredging operations. In: Chemistry of Marine Sediments, T.F. Yen (ed.), Ann Arbor Science Publishers Inc., 173-180.

Walker, G., Rainbow, P.S., Foster, P. and Holland, D.L. (1975). Zinc phosphate granules in tissue surrounding the midgut of the barnacle, _Balanus balanoides_. _Marine Biology_ _33_, 161-166.

Watling, H.R. and Watling, R.J. (1976). Trace metals in oysters from Knysna Estuary. _Marine Pollution Bulletin_ _7_, 45.

Willey, J.D. (1977). Coprecipitation of zinc with silica in seawater and in distilled water. _Marine Chemistry_ _5_, 267-290.

Windom, H.L. (1975). Environmental aspects of dredging in the coastal zone. In: _Critical Reviews in Environmental Control_, C.P. Straube (ed.) _6_, 91-109.

Wolfberg, A., Kahanovich, Y., Avron, M. and Nissenbaum, A. (1980). Movement of heavy metals into a shallow aquifer by leakage from sewage oxidation ponds. _Water Research_ _14_, 675-679.

Wood, J.H., Rasen, C.J. and Kennedy, S.F. (1968). Synthesis of methyl mercury compounds by extracts of a methanogenic bacterium. _Nature_ _220_, 173.

Zirino, A. and Yamamoto, J. (1972). A pH dependent model for the chemical speciation of copper, zinc, cadmium and lead in seawater. _Limnology and Oceanography_ _17_, 661-671.

Zitko, V. and Carson, W.V. (1972). Release of heavy metals from sediments by nitrilotriacetic acid (NTA), _Chemosphere_ _3_, 113-118.

APPENDICES

Appendix A.   Water Quality Conditions in Sediment Microcosms.

Table Al. Water Quality in High Organic Sediment Microcosm Under Oxic Conditions[1]

Parameter	Fresh Water Initial	Fresh Water Final	50% Seawater Initial	50% Seawater Final	75% Seawater Initial	75% Seawater Final	Seawater Initial	Seawater Final
Salinity (o/oo)	0.0	0.0	-	14.1	20.8	20.8	29.4	28.9
Conductivity (μS/cm)	226	-	-	23.2×10^3	34.2×10^3	33.3×10^3	45.2×10^3	44.5×10^3
pH	7.0	7.8	7.9	7.98	7.95	8.02	7.82	8.08
True Color (mg/1Pt)	40	20	10	10	5	7	0	-
Turbidity (JTU)	7	17	10	.6	.65	.2	0.7	0.1
Total Solids	170	175	15287	15400	23900	24900	34400	34300
Dissolved Solids	131	168	15284	14900	-	-	-	-
Alkalinity (mg/1 $CaCO_3$)	80	71	86	88	104	79	102	93
Acidity (mg/1 $CaCO_3$)	15.4	4.0	7.5	-	-	-	-	-
Hardness(mg/1 $CaCO_3$)	77	80	2780	2650	4030	3920	5450	5400
Calcium	27	27	249	184	276	240	356	-
Total Inorganic Carbon	16	14	18	16	19	16	23	-
Total Organic Carbon	9	12	10	6	23	22	24	-
Chloride	17.4	17.8	8309	7780	11500	11500	16300	16000
Nitrate-N	1.75	1.30	1.03	1.65	1.20	.95	0.88	0.42
Sulphate	17	11	1030	1030	1580	1850	2750	2560

1 all values in mg/1 unless stated differently. The values are results of individual measurements.

Table A2. Water Quality in High Organic Sediment Microcosm Under Anoxic Conditions[1]

Parameter	Fresh Water Initial	Final	50% Seawater Initial	Final	75% Seawater Initial	Final	Seawater Initial	Final
Salinity (o/oo)	0	0	14.8	14.3	22.0	21.8	26.8	27.3
Conductivity (μS/cm)	135	195	24.4×10^3	23.9×10^3	35.1×10^3	33.0×10^3	39.8×10^3	41.8×10^3
pH	6.71	7.60	7.72	7.92	7.88	8.33	7.90	8.88
True Color (mg/1Pt)	20	20	10	15	7	5	2	-
Turbidity (JTU)	14	0.8	0.8	2.2	2.5	1.0	1.5	0.6
Total Solids	163	129	16500	16900	-	-	-	-
Dissolved Solids	137	128	15800	-	25900	22600	28900	30500
Alkalinity (mg/1CaCO$_3$)	40	65	91	76	90	75	97	90
Acidity (mg/1CaCO$_3$)	15	-	-	-	-	-	-	-
Hardness (mg/1CaCO$_3$)	60	66	2800	2750	4200	4200	5150	4900
Calcium	22	-	192	196	276	-	-	-
Total Inorganic Carbon	9	12	16	16	19	18.5	24	-
Total Organic Carbon	8	6	6	3	4	1.2	1.2	4.0
Chloride	13	-	8220	7910	12200	11700	14300	15100
Nitrate-N	1.37	0.47	0.52	0.48	0.75	0.40	0.69	0.38
Sulphate	17	15	1060	1240	1880	1870	2400	2480

1. All values in mg/1 unless stated differently. The values are results of individual measurements.

Table A3. Water Quality in Low Organic Sediment Microcosm Under Oxic Conditions[1]

Parameter	Fresh Water Initial	Fresh Water Final	50% Seawater Initial	50% Seawater Final	75% Seawater Initial	75% Seawater Final	Seawater Initial	Seawater Final
Salinity (o/oo)	0	0	-	14.7	22.4	21.9	29.4	28.9
Conductivity (μS/cm)	150	-	-	24.6×10^3	35.2×10^3	34.9×10^3	45.2×10^3	44.6×10^3
pH	7.45	7.72	-	7.98	7.93	8.12	7.82	8.09
True Color (mg/1Pt)	10	10	5	10	5	7	0	-
Turbidity (JTU)	27	1.4	2.5	0.5	0.5	0.2	0.7	0.1
Total Solids	153	149	15274	16600	24800	25900	34400	32500
Dissolved Solids	99.1	144	15272	16100	23800	-	-	-
Alkalinity (mg/1CaCO$_3$)	60	48	75	65	91	75	102	92
Acidity (mg/1CaCO$_3$)	1.5	2.0	6	-	-	-	-	-
Hardness (mg/1CaCO$_3$)	45	43	2761	2780	4100	4150	5450	5500
Calcium	14	17	244	240	284	250	356	-
Total Inorganic Carbon	15	6	14	11	16	13	23	-
Total Organic Carbon	19	12	21	13	4	4	1	-
Chloride	17	18	8309	8140	12400	12100	16300	16000
Nitrate-N	1.31	1.28	1.02	1.50	1.18	1.07	0.88	0.50
Sulphate	14	9	1070	1080	1630	1900	2750	2520

1 all values in mg/1 unless stated differently. The values are results of individual measurements.

Table A4. Water Quality in Low Organic Sediment Microcosm Under Anoxic Conditions[1]

Parameter	Fresh Water Before	Fresh Water After	50% Seawater Before	50% Seawater After	75% Seawater Before	75% Seawater After	Seawater Before	Seawater After
Salinity (o/oo)	0	0	14.3	14.6	21.5	21.4	26.8	26.9
Conductivity (μS/cm)	149	167	24.7×10^3	23.9×10^3	34.9×10^3	32.6×10^3	39.8×10^3	41.4×10^3
pH	7.08	7.98	7.75	8.35	7.98	7.87	8.08	8.10
True Color (mg/l Pt)	10	50	50	20	9	6	2	-
Turbidity (JTU)	27	2.5	1.6	7.0	9.5	13	2.6	0.2
Total Solids	135	-	16100	17300	-	-	-	-
Dissolved Solids	87.2	107	15500	-	26500	22900	29400	28800
Alkalinity (mg/l $CaCO_3$)	38	58	96	61	82	72	97	94
Acidity (mg/l $CaCO_3$)	1.5	-	-	-	-	-	-	-
Hardness (mg/l $CaCO_3$)	53	56	2780	2650	4000	4000	5100	4900
Calcium	18	19	196	192	272	-	-	-
Total Inorganic Carbon	8	9	17	10	17	17.5	24	-
Total Organic Carbon	6	7	5	7	4	2.5	1.2	4.5
Chloride	12	-	7920	8060	11900	11700	14600	14900
Nitrate - N	1.58	0.67	0.75	0.63	0.75	0.65	.61	.56
Sulphate	12	10	1060	1240	1780	1420	2180	2580

1. All values in mg/l unless stated differently. The values are results of individual measurements.

Table A5. Water Quality in High Organic Sediment Microcosm at Different pH's[1]

Parameter	pH = 5 Initial	pH = 5 Final	pH = 7 Initial	pH = 7 Final	pH = 10 Initial	pH = 10 Final
Conductivity (μS/cm)	3680	3930	203	284	11100	10900
pH	4.90	5.08	7.25	8.23	9.99	9.75
True Color (mg/l Pt)	10	25	7	15	10	500
Turbidity (JTU)	4.7	18	3.6	12	72	1.3
Dissolved Solids	3330	3970	-	-	9000	8430
Alkalinity (mg/l $CaCO_3$)	1250	1600	66	121	7900	7500
Acidity (mg/l $CaCO_3$)	1620	1010	-	-	-	-
Hardness (mg/l $CaCO_3$)	-	-	76	120	-	-
Total Inorganic Carbon	0	-	15.5	-	1100	-
Total Organic Carbon	1670	1750	2	7.5	0	48.5
Chloride	13.8	15.6	8.3	15.6	11.7	16.7
Nitrate - N	6.16	4.97	1.55	1.67	11.9	15.5
Sulphate	19.2	-	16.3	5.7	-	-

1. All values in mg/l unless stated differently. The values are results of individual measurements.

Table A6. Water Quality in Low Organic Sediment Microcosm at Different pH's[1]

Parameter	pH = 5 Initial	Final	pH = 7 Initial	Final	pH = 10 Initial	Final
Conductivity (μS/cm)	3340	3080	142	125	12×10^3	10.6×10^3
pH	4.93	5.54	6.90	7.90	10.0	10.0
True Color (mg/l Pt)	20	20	20	20	20	450
Turbidity (JTU)	6	30	5	0.6	23	1.4
Dissolved Solids	4300	3180	-	-	12000	8190
Alkalinity (mg/l $CaCO_3$)	950	1300	40	41	7710	7350
Acidity (mg/l $CaCO_3$)	1430	324	-	-	-	-
Hardness (mg/l $CaCO_3$)	50	-	50	48	28	-
Calcium	16	-	16	-	3.2	-
Total Inorganic Carbon	0	0	8	11	1120	-
Total Organic Carbon	1500	1350	4	2	3.0	48
Chloride	7.5	9.7	9.0	8.3	7.5	13.1
Nitrate - N	5.3	3.2	1.45	1.18	11.8	15.0
Sulphate	15.2	16.8	13.5	12.7	-	-

1. All values in mg/l unless stated differently. The values are results of individual measurements.

Appendix B. Effect of pH on Trace Metal Exchange

Table B1. Effect of pH 5 on Trace Metal Exchange in Sediment

TIME (days)	COPPER		IRON		LEAD		ZINC		TURBIDITY	pH
	D	P	D	P	D	P	D	P		
HIGH ORGANIC (WILLINGDON)										
0	38	7	138	610	76	7	25	3	5	4.90
1	110	153	16000	9240	1000	650	1030	189	110	5.03
2	142	51	11700	4440	1000	276	1100	67	52	5.03
3	158	9	7560	2370	950	72	1200	13	13	-
4	150	3	5900	1420	840	42	1250	4	7	-
5	158	3	5200	960	790	37	1300	4	6	4.97
6	146	2	5200	830	780	29	1320	3	-	-
7	142	2	5300	840	660	34	1350	2	9	5.06
10	128	3	6600	1580	560	58	1470	13	17	5.10
13	-	4	-	3090	-	96	-	7	-	-
26	85	5	8960	12500	260	146	1780	86	57	5.50
34	63	2	2710	22500	530	48	2400	28	23	4.93
LOW ORGANIC (GILMORE)										
1	33	28	173	1420	200	47	28	28	73	4.93
3	41	7	119	590	227	17	35	7	22	4.93
8	41	6	330	400	253	8	54	6	18	4.85
12	44	4	1220	286	287	7	160	5	15	4.90
19	45	3	2500	380	303	8	228	4	10	5.11
26	36	2	10000	538	254	13	380	1	9	5.17
31	32	4	11500	960	212	15	440	2	15	5.29
34	30	4	8800	4000	140	86	460	3	19	5.40
36	27	4	6800	6010	-	103	490	3	24	5.50

Footnote: D = Dissolved, P = Particulate. All values in µg/l total metal

Table B2. Effects of neutral pH (7) on Trace Metal Exchange in Sediment.

TIME (days)	COPPER		IRON		LEAD		ZINC		TURBIDITY	pH
	D	P	D	P	D	P	D	P		
HIGH ORGANIC (WILLINGDON)										
0	30	7	272	410	6	4	27	4	4	7.25
1	12	332	440	15500	48	1390	24	484	120	7.78
2	11	105	146	3260	27	471	16	180	59	-
3	11	53	102	2110	16	308	13	87	34	-
4	12	10	58	570	14	88	10	21	8	8.15
6	11	8	74	510	12	44	7	14	-	-
7	11	6	148	625	10	30	6	13	7	-
10	11	3	-	694	7	18	5	10	8	8.00
13	9	2	196	715	2	11	3	7	8	7.96
26	6	2	85	1170	1	7	4	44	21	8.20
34	5	2	20	185	1	5	5	-	6	8.22
40	5	5	24	1310	1	12	3	-	-	-
LOW ORGANIC (GILMORE)										
0	24	11	152	470	7	19	34	9	-	-
1	9	84	320	5050	18	159	16	88	113	-
3	9	17	160	810	9	38	5	19	29	7.73
8	8	7	138	182	9	13	6	10	13	7.76
12	8	4	138	270	8	10	5	7	8	-
19	12	3	-	128	-	8	4	2	3	-
28	9	<1	78	12	8	<1	4	1	.6	-
31	10	<1	64	6	9	<1	4	<1	.3	7.82
34	9	<1	66	6	8	<1	4	<1	.3	7.90
36	9	<1	46	10	4	<1	2	<1	.5	7.90

Footnote: D = Dissolved, P = Particulate. All values in µg/l total metal

Table B3. Effect of pH 10 on Trace Metal Exchange in Sediment.

TIME (days)	COPPER		IRON		LEAD		ZINC		TURBIDITY	pH
	D	P	D	P	D	P	D	P		
HIGH ORGANIC (WILLINGDON)										
0	30	15	220	732	4	23	10	43	72	9.99
1	72	182	392	6860	773	945	16	343	120	9.92
2	68	147	262	6850	704	858	18	282	89	
3	68	51	456	1600	272	426	16	82	35	
4	52	35	448	1050	194	362	14	43	13	
5	58	24	-	470	192	178	16	28	8	
6	72	21	444	350	230	130	16	23	-	
7	78	20	484	310	240	120	16	20	5	
10	82	20	·618	280	320	118	24	20	4	
13	92	14	740	320	322	117	26	21	3	
26	150	14	910	248	450	104	45	36	3	
34	220	9	1020	290	450	99	55	29	2	
LOW ORGANIC (GILMORE)										
0	29	11	200	580	16	23	7	38	-	
1	60	57	240	4790	50	199	16	103	56	
2	77	18	300	1330	52	70	14	39	25	
5	80	11	400	847	52	35	15	26	14	
8	82	7	400	585	43	30	21	15	5	
12	84	6	416	428	60	27	12	13	4	
19	102	5	452	340	60	24	-	7	3	
28	89	2	440	187	62	17	13	5	2	
31	88	2	510	170	62	16	14	4	2	
34	90	4	576	160	56	17	12	5	2	
36	92	3	552	168	59	14	13	4	1	

Footnote: D = Dissolved, P = Particulate.   All values in μg/l total metal.

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Appendix C. Trace Metal Levels in Benthic Invertebrates.

Table C1 : Trace Metal Levels in Benthic Invertebrates in Laboratory Microcosms[1]

Organism	Sampling Interval (days)	Copper		Iron		Lead		Manganese		Zinc	
		H	L	H	L	H	L	H	L	H	L
Amphipods	0	162		550		204		22.8		83.1	
	7	142	140	1230	3280	200	182	72.8	109	115	111
	14	158	153	3080	3890	214	150	119	159	119	105
	28	180	168	4030	4900	222	122	366	561	135	100
Chironomids	0	23		5320		35.4		92.1		106	
	5	-	61.3	-	6280	-	143	-	275	-	123
	9	51.5	-	5760	-	153	-	101	-	168	-
	18	-	66.1	-	7290	-	116	-	301	-	156
	28	42.1	91.7	7420	7340	110	121	150	422	152	181
	42	68.1	124	19,100	7470	286	159	266	368	211	199
Oligochaetes	0	26.7		7130		167		99.3		147	
	7	24.5	15.4	1270	1280	132	30.9	37.8	50.9	153	130
	14	34.3*	35.4	2225*	4440	248*	87.5	41.8*	113	162*	169
	28	64.4	34.5*	3130	5575*	447	122.5*	58.4	140*	233	196.5*
	42	20.5*	60.1*	809*	3655*	168*	100.2*	30.3*	83.3*	139*	136.5*
Opossum	0	-	27.4	-	383	-	<7.8	-	43.8	-	64.9
Shrimp	7	-	86.1	-	930	-	19.8	-	213	-	69.2

1. All values represent total metal in ppm (mg/kg) dry weight of organisms.
   H = High organic sediment, L = Low organic sediment

* Average values for two sets of organisms sieved from separate microcosm containers.

LIST OF PUBLICATIONS

Mueller, J.C. and K.S. Bindra (1975). Rotating Disk Looks
    Promising for Plant Wastes. Oil and Gas Journal, 66-68
    January 13.

Keays, J.L., K.S. Bindra, P.F. McDowell and J.V. Hatton (1977).
    Single-Point Procedure for PFI-Mill Evaluation of Softwood
    Kraft Pulps. Tappi 60(6) 81-83.

Bindra, K.S. and K.J. Hall (1977). Geochemical Partitioning
    of Trace Metals in Sediments and Factors Affecting
    Bioaccumulation in Benthic Organisms. Report prepared for
    NRC, Ottawa (contract #032-1082/6073), 59 pp.

Bindra, K.S. and K.J. Hall (1978). Bioaccumulation of
    Selected Trace Metals by Benthic Invertebrates in
    Laboratory Bioassays. Report prepared for NRC, Ottawa
    (contract #032-1082/6073), 25 pp.

Bindra, K.S. and K.J. Hall (1979). Effect of Physical and
    Chemical Factors in Water and Sediments on the Release
    of Selected Trace Metals. Report prepared for NRC, Ottawa
    (contract #032-1082/6073), 54 pp.

Hall, K.J. and K.S. Bindra (1979). Geochemistry of
    Selected Metals in Sediments and Factors Affecting
    Organism Concentrations. A paper presented at the
    International Conference on Management and Control of
    Heavy Metals in the Environment, Imperial College,
    London, Sept. 1979.