CONTRASTING THE GEOCHEMISTRY OF SUSPENDED PARTICULATE MATTER AND DEPOSITED SEDIMENTS OF THE FRASER RIVER ESTUARY: IMPLICATIONS FOR METAL EXPOSURE AND UPTAKE IN ESTUARINE DEPOSIT AND FILTER FEEDERS

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J. R. Pierre Stecko

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NAME: J. R. Pierre Stecko

DEGREE: Master of Science

TITLE OF THESIS: Contrasting the geochemistry of suspended particulate matter and deposited sediments of the Fraser River Estuary: Implications for metal exposure and uptake in estuarine deposit and filter feeders

EXAMINING COMMITTEE:

Chair: Dr. Russell A. Nicholson

Dr. Leah I. Bendell-Young
Senior Supervisor
Assistant Professor of Biological Sciences

Dr. Rolf W. Mathewes
Professor of Biological Sciences

Dr. Ken J. Hall
Professor of Civil Engineering
Westwater Research Centre
University of British Columbia

Dr. Alan G. Lewis
Professor of Oceanography and Zoology
University of British Columbia
External Examiner

Date Approved: Feb 18/97

ABSTRACT

Suspended particulate matter (SPM) and deposited sediment (DS) from depositional environments of the Fraser River Estuary were investigated for one year. Both sediment types and environments were physically and geochemically characterized. The concentrations of Cd, Cu, Fe, Mn, Pb, and Zn in four selective extracts were determined in both SPM and DS. The geochemical nature of the two sediments as they influence the potential bioavailability of sediment-associated metals was considered and the bioavailability of Cd (as ^{109}Cd) from each sediment was assessed.

SPM and DS differ in their geochemical properties. SPM consists of smaller particles and has significantly higher organic, iron oxide, and manganese oxide content than does DS. Concentrations of organic matter and iron oxide in SPM were greatest from November through March which corresponds to the period of low flow in the Fraser River. Concentrations of manganese oxide in SPM were highly variable. These observations manifest themselves in Cd, Cu, Pb, and Zn concentrations much higher in SPM than DS. Significant differences were apparent in the easily reducible, reducible and organic metal fractions, the fractions of most biological relevance. Conversely, concentrations of residual metals were similar in the two sediments. The proportion of reactive Cu and Zn (but not Pb) was significantly greater in SPM than in DS. The proportion of both easily reducible and organic copper and the proportion of easily reducible zinc were greater in SPM than in DS.

The relationship between metal concentrations and the physico-chemical and geochemical features of the sediment were stronger for SPM than for DS. This was particularly true of the easily reducible and organic phases and less true of the residual phase. Iron oxides, manganese oxides, and organic matter were the dominant correlates with SPM metals while pH, organic matter, and manganese oxides were the dominant correlates with DS metals.

At environmentally realistic exposure levels, assimilation efficiency of radiolabelled Cd from spiked SPM and DS was compared in the filter feeding clam *Protothaca staminea*. Identical ^{109}Cd spiking resulted in similar partitioning in SPM and DS. Assimilation efficiency (^{109}Cd retained by the organisms relative to the inert tracer ^{241}Am) was 32.80% ± 2.64 from SPM and 25.16 ± 3.33 from DS (mean ± SE; n=3 exposure systems). Further, in *P. staminea* and *Macoma balthica*, 79-91% of ^{109}Cd uptake occurred by the particulate phase versus 9-21% from the water, with the proportion of particulate uptake being directly related to the extent of isotope desorption from spiked sediments.

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CHAPTER 1: INTRODUCTION

Scientific understanding of metal association and behaviour in aquatic systems is dependent upon geochemistry. Uptake of metals by organisms is also influenced by geochemical factors. Current focus on factors that influence trace metal behaviour and effects stems from the increased fluxes of trace metals from terrestrial and atmospheric sources to the aquatic environment as mankind's activities intensify (Forstner and Wittman, 1981). In a pragmatic sense, to effectively manage aquatic ecosystems, we need to understand the spatial distribution and forms of contaminants, and where and when these contaminants can become available to organisms. Understanding of their geochemical controls is therefore required.

It is widely recognized that the behaviour, transport, and fate of metals in aquatic systems are determined by the nature of their association with particulate matter (Warren and Zimmerman, 1994; Douglas et al., 1993; Regnier and Wollast, 1993; Horowitz et al., 1990; Honeyman and Santschi, 1988). The nature of such associations and the subsequent behaviour and fate of metals in aquatic systems is determined by a wide variety of physico-chemical and geochemical features of a system of interest. The biological relevance of metal geochemistry is several fold. Biological uptake, which is a prerequisite for effects, is intimately dependent on the geochemistry of aquatic particles. The geochemistry of aquatic particles (sediments) will determine the presence and form of trace metals in the environment surrounding a variety of organisms. This effectively dictates what an organism can come into contact with in it's environment. In addition, the physical form of the metal (geochemical association) interacts with the uptake capabilities of an organism to dictate the subset of metals that are available (in free form or released from particulates). A specific example of this, on which this research is focussed is the case in which particulates (deposited sediment and suspended particulate matter), with their variable geochemical characteristics actually provide a food source to aquatic invertebrates.

The following dissertation considers and contrasts the geochemistry of suspended particulate matter (SPM) and deposited sediments (DS) in an estuarine environment whose physico-chemical characteristics are considered concurrently. A comparison of metal uptake from SPM versus DS is considered in two particle feeding species. The detailed objectives of this work are provided in section 9 of this introduction. The purpose of this introduction is to provide the rationale for this work, expand on the basic premises outlined above, and provide information required to understand trace metal interactions in the aquatic environment and their biological implications, with specific emphasis on particle feeders.

The introduction puts the research into context for the reader by reviewing some basic concepts of metal input and behaviour in aquatic systems, metal interactions with biota, unique properties of the estuarine environment, and introduces the rationale and objectives of this research. Chapter 2 provides a more detailed summary of the current state of the science of metal geochemistry and bioavailability. Chapter 3 presents the methods used throughout the study. Chapter 4 presents and discusses the findings on the physico-chemical and geochemical features of the Fraser River Estuary and the concentrations of metals in different phases of SPM and DS of the Fraser River Estuary. Chapter 5 considers the physico-chemical and geochemical factors that most influence metal concentrations in SPM and DS. Chapter 6 presents and discusses the assimilation of radiolabeled Cd from SPM and DS and Chapter 7 synthesizes the findings, summarizes the conclusions, and considers the geochemical and biological implications of the findings. Definitions and abbreviations used in the text are provided in Appendix I; Appendix II summarizes metal detection conditions; and Appendix III summarizes sediment metal concentrations by month.

1.0 METALS IN THE AQUATIC ENVIRONMENT

Metals are natural components of the aquatic environment. However, human activities have drastically altered the environmental concentrations of many metals. Nriagu and Davidson (1986) estimate the global anthropogenic enrichment of Cd and Pb at 7.6 and 24.1 times, respectively. Bryan (1976) estimated the anthropogenic mobilization of metals relative to natural mobilization as: Cu - 12 to 16; Fe - 13 to 16; Mn - 3.6 to 19; Pb - 13 to 18; and Zn - 11 to 14. Recent control technologies may be decreasing these ratios (Foster and Charlesworth, 1996); however, anthropogenic mobilization makes up a large component of total release to the aquatic environment.

Natural sources of metals include wind blown soils, volcanic eruptions, sea spray, forest fires, biogenic aerosols, and a variety of weathering processes (Nriagu, 1989). Anthropogenic sources include transportation, industry, mining, municipal and agricultural wastes and dump leachates (Foster and Charlesworth, 1996). Anthropogenic introduction of metals into the environment is often the result of the use of modern industrial products such as the weathering and flaking of paints; the incineration of pharmaceuticals, batteries, plastics, and electrical goods; wear and weathering of electroplated surfaces, plastics, leather and tires; the decomposition of treated wood; and the combustion of fuels (Tarr and Ayres, 1990).

2.0 WATER, SEDIMENTS, AND METALS

Determining the significance of metals in aquatic systems depends on our ability to quantify the spatial and temporal trends in metal transport and geochemical association. Metals in the aquatic environment are distributed between the dissolved and particulate (sediment) phases. Adsorption/desorption phenomena at the solid-solution interface are significant controls on the fate of contaminants in the hydrosphere (Bourg, 1989), therefore the behaviour of metals in natural systems is profoundly influenced by the presence of particle surfaces (Honeyman and Santschi, 1988). Foster and Charlesworth (1996) note the particular significance in quantifying the spatial and temporal trends in metal transport and in assessing the relative significance of various heavy metal pathways in the partitioning of metals between suspended particulates and water, the mechanisms by which heavy metals are retained in the particulate fraction, and the post-depositional stability of sediment-associated metals within the river corridor.

Generally, more than 90% of the heavy metal load in aquatic systems is bound to particles like suspended matter or sediments (Calmano et al., 1993). Metal concentrations in the fine-grained sediments of river systems can be more than 100,000 times higher than the dissolved concentrations of the same metal (Horowitz, 1991). Yet, most freshwater and seawater systems show undersaturation with respect to solid phases (Campbell and Tessier, 1989). This suggests that solid surfaces influence trace metal fate. Thus, the distribution of metals between dissolved and particulate forms has been, and continues to be of scientific interest. Some understanding has been gained and generalizations can be made, although the distribution of metals will differ greatly in different systems. Campbell and Tessier (1989) note the following strength of metal binding to generalized particles: Pb > Cu > Zn > Cd. Meybeck and Helmer (1989) provided an extensive review of the distribution of metals among dissolved and particulate phases in rivers. They determined the dissolved transport index (DTI); the percentage of total metal that is found in the dissolved phase. They rank metals according to DTI as: Zn < Fe < Pb < Mn < Cd < Cu. The DTI for these metals are 0.1-0.5% for Zn and Fe, 0.5-1.0% for Pb, 1.0-5.0% for Mn and Cd and 5.0-10% for Cu. The authors emphasize that these data should only be used as a rough estimate of the dissolved/particulate distribution in rivers and estuaries; the actual values vary widely among estuaries and are influenced by many factors as summarized in section 5.

Closer consideration of the distribution of metals reveals a heterogeneity of metal forms in aquatic systems. The aquatic chemistry of trace elements is ruled by homogenous chemical reactions (e.g., acid-base, complexation with inorganic ligands such as CO_3^{2-}, OH^-, Cl^-, S^{2-}, or organic matter such as humic substances or biological ligands, oxidation-reduction, and chemical precipitation) and surface reaction involving colloids, particulates, and sediments (Astruc, 1989). Some of the variety of reactions that occur in aquatic systems are summarized in section 5. This heterogeneity results in various states of mobility, leachability and bioavailability and has implications on metal transport and fate, and on the biological significance of metals (chapter 2).

Historically, the focus of metal studies in aquatic systems has been upon water. Metals in water were divided into dissolved (filtered) and "total" (unfiltered, dissolved and particulate). As is evident from the preceding paragraphs, this provided a limited picture of the distribution of metals in aquatic systems. Metals associated with aquatic particles have been considered in less detail, and focus has generally been on deposited sediments. This is generally the result of the difficulties involved in the collection of suspended particulates (Ongley and Blachford, 1982; Horowitz et al., 1989; Burrus et al. 1989). However, suspended particles may represent the most relevant fraction from a chemical and biological viewpoint due to their direct interface with the water, their high surface area to volume and their high nutritive quality relative to deposited sediment (Hart, 1982; Ongley et al.; 1982, 1988, 1992; Horowitz, 1986; Tessier and Campbell, 1987; Warren, 1994). Benthic organisms that ingest particles also tend to select and ingest the smaller, lighter particles in their environment

(Campbell and Tessier, 1996). This is designed to maximize the ingestion of organic carbon in the form of attached bacteria and/or surface bound organic coatings, since small particles have very high surface areas relative to their volume. However, due to the high surface to volume ratios and the characteristics of surface materials, this can also result in the ingestion of the very particles that tend to be enriched in metals. Suspended particulates (suspended sediments) therefore represent important potential sources of metals to aquatic organisms (discussed next section), yet have seldom been considered. Studies that have collected and analyzed suspended sediments as entities separate from water and deposited sediments have found that many heavy metals and organic contaminants are partially to wholly transported in association with suspended matter (Ongley et al., 1982; Wollast, 1982; Regnier and Wollast, 1993). Therefore, as pointed out by Ongley et al. (1988), the current focus of chemical monitoring efforts on water and bottom sediments is, in many cases, misguided. Suspended particulate matter (SPM) could be a more appropriate material in which to monitor aquatic contaminants (Ongley et al., 1988).

3.0 BIOLOGICAL SIGNIFICANCE OF METALS IN AQUATIC SYSTEMS

Metals are of concern in aquatic systems due to their interactions with organisms. Elevated metal levels are of interest due to their possible role in exerting some type of effect on organisms. Effects are defined as the impairment of function at any level of biological organization. This definition is appropriate since it is believed that a subsidy at one level of organization (i.e., individual) will often cause impairment of function at another (i.e., community). In such circumstances, for example, the presence of elevated metal levels could be important in limiting the distribution of organisms.

The role of suspended particulates in metal interactions with aquatic organisms is of particular importance when their geochemical properties and nutritional qualities are considered. Organisms live in contact with both dissolved and particulate trace metals and can, in principle, obtain trace metals either directly from the water or through ingestion of solid phases (Campbell and Tessier, 1989). One important feature of SPM is that it represents nutritionally desirable material for many deposit and filter feeders. This is generally due to it's high content of detritus and associated bacterial populations (Hart, 1982; Tessier and Campbell, 1987; Douglas et al., 1993; Rao et al., 1993). Thus, SPM dynamics in aquatic systems can control metal-organism interactions in two ways: 1) by controlling the distribution of metals between dissolved and particulate phases, and 2) by being a desirable food source whose ingestion can result in metal uptake.

An important pathway for the exertion of effects by metals in aquatic systems involves exposure and uptake into sensitive biological compartments. Metal uptake is therefore an important process potentially leading to effects. It is also a process amenable to scientific study. A large number of physico-chemical and geochemical factors interact to influence exposure and uptake; these factors are collectively included in the study of "geochemistry" (Chapter 2). The interface of ambient geochemistry with the organism influences the metal that is actually taken up, or the "bioavailable" metal fraction (Chapter 2). Different metals have varying toxicities to aquatic organisms. Among the metals considered in this document, iron is considered a macronutrient; manganese, zinc, and copper are micronutrients; and lead and cadmium serve no biological function. Wood (1974) classifies Cd, Cu, Pb, and Zn as very toxic and relatively accessible elements. Toxicity of these metals increases in the order Zn < Cu < Pb < Cd (Ketchum, 1980). Although toxic mode of action will vary from metal to metal, generally, at elevated levels, metals act as enzyme inhibitors in organisms. For example, copper, cadmium and lead can inhibit enzyme activity by forming mercaptides with their sulfhydryl groups (Johnston, 1976).

Because metals in sedimentary environments occur in both dissolved and particulate states in a variety of chemical forms, the total concentration of a metal is rarely useful in determining it's biological availability (Campbell et al., 1988). Careful attention to the forms of metal in the environment has led to recent advances in understanding the subset of metals that can be taken up by aquatic life. In the aquatic environment, a practical division of metals is into metal associated with suspended particles (SPM), settled particles (deposited sediment), and dissolved metal. This practicality stems from the ease with which organisms can be effectively divided into groups which are exposed to one or more of these vectors. Chemical aspects of a metal's association with particles is only part of the puzzle of biological uptake. Biological characteristics interact with chemical factors. Therefore, any process that changes the distribution of metals between the phases has repercussions upon metal uptake by different organisms. All phases represent potentially important routes of metal uptake and are all interconnected. In monitoring to determine the biological significance of trace metals, more emphasis must be put on matching the exposure characteristics of organisms with the material monitored. In many cases, organisms may be preferentially ingesting SPM, and living in water whose dissolved metal concentrations are controlled by SPM. A large scientific literature has developed around relating metal concentrations and geochemical characteristics (and sometimes partitioning) in bottom sediments to metal levels in (or toxicity to) organisms with little consideration of how the organism responds to it's environment, or even what vector (deposited sediment, suspended particulates, or water) most directly determines uptake and accumulation.

4.0 ASSESSING METAL GEOCHEMISTRY AND AVAILABILITY

Many methods have been developed by the scientific community to assess the significance of particle-associated metals in aquatic systems. These methods fall into two broad categories: chemical, which attempt to determine bioavailability based upon geochemistry; and biological in which exposures are conducted under varying conditions and can be related to geochemistry. Both are in common use, though many researchers point out their limitations (i.e., Tessier and Campbell, 1987; Rainbow et al., 1990).

4.1 Chemical Extractions

Chemical extractions can be used to divide heterogenous sediments into operationally defined components. Two approaches attempt to determine how (the mechanistic approach) and where (the phase approach) metals are associated with sediments (Horowitz, 1991). The mechanistic approach considers how metals are retained in or on sediments. This includes adsorption, precipitation, coprecipitation, organometallic bonding, and incorporation into the crystalline matrix (Horowitz, 1991). The phase approach considers the different sediment phases that the metal associates with. These phases include interstitial water, clay minerals, carbonates, organic matter, oxides, sulphides, and crystalline. Very few attempts to chemically partition complex sediments entail purely mechanistic or phase approaches, rather they combine both (Horowitz, 1991).

Chemical extractions have been designed to extract specific sediment phases (phase approach) to assess potential metal availability from sediments (Tessier et al., 1979; Bendell-Young et al., 1992). Essentially, these attempt to determine the geochemical associations of metals (exchangeable, Mn oxide bound, Fe oxide bound, organic bound, and residual). These methods are necessarily operationally defined and are criticized for not being sufficiently specific (Kheboian and Bauer, 1987; Nirel and Morel, 1990; Tack and Verloo, 1995) and for metal redistribution during extraction (Rendell et al., 1980). However, several experiments have verified their specificity (Tessier and Campbell, 1988; Belzille et al., 1989; Warren and Zimmerman, 1994) and they are valuable in providing insight to the potential availability of metals. In addition, these extractions have merit on the logic that the easier the release, the greater the potential for organism uptake. The use of these different extractants has provided better prediction than total metal concentrations by approximating metal accessibility to organisms (Tessier et al., 1994). Many authors, while cautioning on the uncritical use of selective extractions, also note that it is the best means of predicting the long term effects of contaminated sediments and of predicting relationships between metal burdens in benthic organisms and their sedimentary environment (i.e., Forstner, 1993; Tack and Verloo, 1995). These methods are only applicable to oxic sediments, and should always be clearly identified as "operationally defined".

4.2 Biological Exposure

The use of organisms and their assemblages to interpret the biological significance of metals generally falls into two categories: laboratory and field studies. Laboratory studies consist of simple exposure under carefully controlled manipulated conditions; field observation uses information on accumulated metal. It has become increasingly evident that to gain an effective understanding of the biological significance of metals in aquatic systems, both geochemical and biological methods must be considered. In this manner, knowledge has been gained on the key relationship between bioavailability and geochemistry.

Biological uptake experiments using radiotracers have proven very useful in providing a means of determining assimilation efficiency. Assimilation efficiency is operationally defined here as **the**

efficiency with which an element of interest is retained by an organism relative to an inert tracer with a similar gut passage time as determined by the twin tracer method of Fisher and Reinfelder (1991). In a strict sense this method provides no indication of whether the element of interest is assimilated, and the literature reveals a disagreement on semantics with respect to retention, absorbtion, and assimilation. These terms are often used synonymously with the assumption that retention efficiency accurately represents assimilation efficiency. In practice, these techniques can reveal much information about metal bioavailability and it's relation with a variety of physico-chemical and geochemical factors (which can be manipulated). However, retained, absorbed, and assimilated metal may be eliminated by organisms over time.

Several researchers have furthered our understanding by comparing assimilation of radiotracers to carefully monitored geochemical characteristics. The experiments of Luoma (Luoma and Jenne, 1976, 1977; Harvey and Luoma, 1985a, 1985b; Luoma et al., 1992) isolate particulate from solute metal uptake in *Macoma balthica*, and relate particulate uptake to geochemical phase. In these experiments, clams were fed with whole sediments or distinct geochemical phases (Fe oxides, Mn oxides, organics, carbonates) spiked with metals, while control clams were kept in dialysis bags. Experiments using different complexing agents in exposure tests have proven useful in determining that exposure to free metal ion is the predominant route of bioavailability and toxicity to many organisms. Toxicity of metals determined with "standard" protocols is essentially an attempt to assess metal bioavailability although this is seldom considered explicitly. A wealth of toxicity test data demonstrates for both metals and organics that due to geochemical and biological factors, similar concentrations of a given chemical in two different sediment types most often do not produce the same result; and for metals can be off by orders of magnitude (Adams et al., 1992). Similarly, when comparing different sediments in uptake and/or assimilation experiments, differences can be due as much to partitioning as to actual differences in uptake from sediments through the gut (Luoma, 1983). For this reason, mechanistic understanding requires separation of solute and particulate uptake.

Field studies generally make use of simultaneously collected environmental samples (sediment, pore water, and overlying water) and attempt to determine the "bioavailable" fraction by correlation analysis. This approach has improved our knowledge of geochemical control of metal uptake (i.e., Tessier et al., 1983; 1984; Bendell-Young and Harvey 1991a; 1991b; 1992; Bendell-Young et al., 1994) and has identified the sediment phases that are important in influencing trace metal bioavailability. The present study uses the technique of assimilation efficiency to assess the uptake of metals from estuarine sediments that are geochemically characterized according to the findings of such previous studies. This method provides the most direct measure of bioavailability under carefully monitored conditions.

5.0 METALS AND THE ESTUARINE ENVIRONMENT

An estuary is "a semi-enclosed coastal body of water, which has a free connection with the open ocean, and within which seawater is measurably diluted with freshwater derived from land drainage" (Pritchard, 1967). The variable nature of the estuarine ecosystem provides a unique set of challenges for biota. In addition, the physical and chemical variability provides an interesting case study in metal geochemistry in a system with a high suspended particulate concentration.

5.1 The Fraser River Estuary

The Fraser River Estuary drains 25% of the total land mass of B.C., or approximately 230,000 km^2 (Dorcey and Griggs, 1991). It is the greatest producer of salmonids of any single river in the world (Northcote and Larkin, 1989). Its mean suspended particulate concentration generally varies spatially and temporally from 135 to 186 mg/L in the estuarine regions. During freshet, when flow is several orders of magnitude above base, suspended particulate concentrations can reach mean values of 400 mg/L, with near-bottom concentrations approaching 1000 mg/L (Milliman, 1980). The Fraser River is a partially mixed salt wedge estuary where the lighter freshwater (river flow) runs over the heavier salt water, which encroaches along the bottom of the estuary allowing the intrusion of marine organisms further upstream than water salinity would predict (McLusky, 1989).

The tidal amplitude of the Fraser River is ca. 3.1 metres; river discharge varies from 400 m^3/s just prior to the spring snowmelt to as great as 15,000 m^3/s in June following a rapid snowmelt, with an average of approximately 3475 m^3/s (Kennett and McPhee, 1989). Most of the sediment transport occurs during the freshet. When river flow is low, incoming tides can cause flow reversal. In many estuaries, the sediments are dominated by the marine influence. However, the Fraser River carries a large suspended particulate load (20 million tonnes are deposited annually in the delta; Hoos and Packman, 1974), and as a result the sedimentary material of the upper and mid estuarine regions is dominated by the river.

Sources of metals to the Fraser include municipal and industrial discharges, as well as non-point source runoff. The lower Fraser receives 2 million m^3 of wastewater each day (Kennett and McPhee, 1988). Industrial waste sources include chemical, concrete, food, forest, gravel washing, metal fabricating and finishing, port industry, and others which discharge approximately 300,000 m^3/d (Environment Canada, 1992), and municipal loading (which contains Fe, Cu, Pb, and Zn) is ca. 850,000 cubic metres per day (Kennett and McPhee, 1988). There are three primary sewage outfalls in the lower Fraser, two of which discharge to the Main Arm. During heavy rainfalls in periods of low flow, 5% of the Fraser River flow can be from contaminated sources (Kennett and McPhee, 1988).

5.2 Physico-Chemical

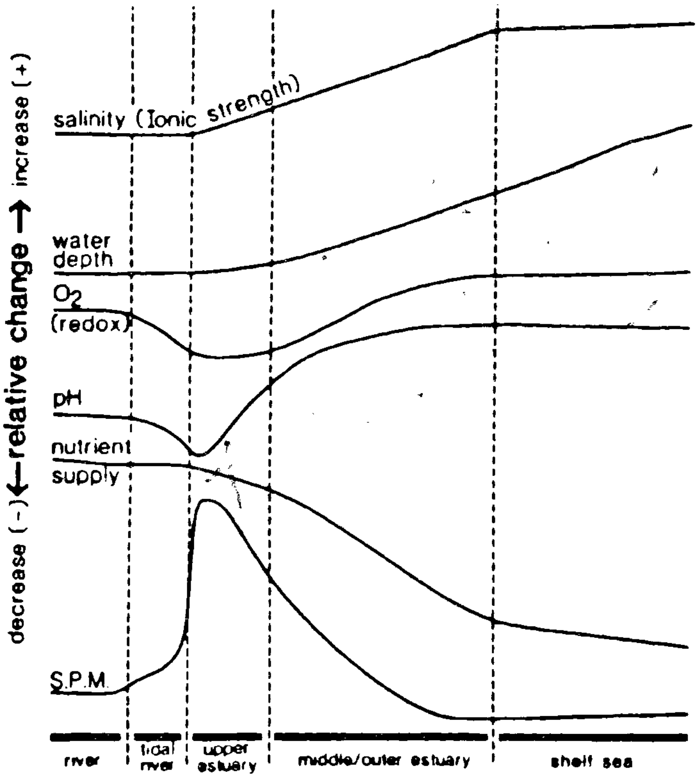
Estuaries are characterized by having a constantly changing mixture of salt and fresh water, and being dominated by fine sedimentary material that can be carried into the estuary from both the river and sea depending upon the physical conditions at a specified location in an estuary. This fine material accumulates on the tidal mudflats of the estuary. In the upper regions of estuaries, where chemical reactions are constrained by short hydraulic retention times, equilibrium will not be reached for kinetically slow removal or release reactions (Millward et al., 1992). In lower estuarine reaches (quiescent zone), equilibrium conditions can occur due to longer flushing times. Because metals are associated with particulate transport, their dispersal through estuarine systems is a function of hydraulic conditions which control sorting (according to differences in particle density and size), mixing processes, where contaminated and uncontaminated sediments are added to the system, and storage and deposition (Foster and Charlesworth, 1996).

Tidal amplitude, river runoff volume, particulate load and size distribution are factors controlling the deposition of particulate material within the estuary. These factors vary considerably among estuaries, making generalizations difficult. A natural sorting according to particle size occurs with the meeting of freshwater and seawater which provides a quiescent zone, allowing the suspended particles to settle. The actual area of settling and suspended particulate concentration varies with both tides and river flow, and as a result varies both semi-diurnally (tidal influence) and seasonally (river influence) and can cover a large area. Suspended particulate material (SPM) ranges from the point of solution, through the colloidal, to discrete visible entities (Morris, 1985). The quantity of suspended particulates varies seasonally with river flow, with a maximum occurring during or just prior to peak flow; and with tides. The tidal influence results in two populations of suspended particles: those present throughout the tidal cycle (permanently suspended); and those present as sediment is washed off tidal flats during tide changes (temporarily suspended) (Sholkovitz, 1979). Thus, substantial temporal and spatial variability may exist in the quantity and properties of estuarine SPM.

Most biogeochemical changes involved in the meeting of freshwaters and seawater in estuaries (i.e., pH, flocculation, speciation) occur at very low salinities (1 ppt range) (Morris et al., 1978; Gobeil et al., 1981). These changes occur in a relatively predictable fashion in different estuaries (Figure 1.1). At the quiescent zone created by the meeting of fresh and saline waters, salinity makes particulate matter cohesive and salt flocculation (salinity-induced aggregation) occurs. Flocculation generally begins at salinities of less than 1 ppt, with small suspended particles aggregating to form larger particles. Flocculation occurs on mixing because the seawater cations neutralize negatively charged ligands (including colloids) (Boyle et al., 1977) allowing aggregation and possibly selective precipitation (i.e., Sholkovitz et al., 1978; Morris et al., 1982). In many estuaries, the area of flocculation is clearly detectable as an "estuarine turbidity maximum", an area of intense deposition of mud and silt.

The pH of estuaries can vary within a narrow range of salinities (Figure 1.1). A pH minimum generally occurs in estuaries at salinities of 0.5 to 3 ppt. Mantoura (1987) found that pH decreased from approximately 7.4 to 6.0 over the salinity range 0.5 to 3 ppt, subsequently increasing to approximately 8.0 as salinity increased. Temperature within estuaries varies both temporally and

Figure 1.1 Chemical changes occurring in the estuarine mixing zone (from GESAMP, 1987)



spatially due to the different temperatures of riverine and marine water. Oxygen content of the sediments and the water column are also variable and are again partly controlled by mixing. In the sediments, differences in oxygen content are controlled by the organic content of the sediments. The resulting microbial and detrital activity can result in anoxic sediments in high organic areas, with only a very shallow strip of surficial sediment remaining oxic. The redox potential and the physico-chemical variability noted above have implications for metal speciation and availability (Chapter 2).

5.3 Metal Behaviour in Estuaries

The behaviour of metals in estuaries is intimately linked to the geochemistry of aquatic particles and hydraulic control on particle behaviour and varies from system to system. Settling particles play a dominant role in transferring heavy metals to estuarine sediments (Foster and Charlesworth, 1996). Because many metals are attracted to particle surfaces, it is believed that the trapping processes at the quiescent zone could produce local regions with unacceptably high levels of contamination (Boicourt, 1993).

Particle size changes total surface area, thereby changing adsorption and desorption of contaminants (Burban et al., 1989). Desorption of particulate metals can occur in estuaries due to both the high ionic strength and possibly a pH minimum. However, due to the complexity of estuarine circulation patterns, processes can be difficult to elucidate. In addition, different metals behave differently (Turner and Millward, 1994). As the salinity gradient promotes desorption of metals from suspended solids, flocculation of colloids of iron and manganese oxides enhance adsorption, possibly offsetting desorption (Astruc, 1989).

5.4 Biological

Factors that covary with changing proportions of fresh versus sea water (sediment deposition, pH, redox, organic matter, oxygen, nutrients, contaminants) also influence the distribution of estuarine organisms. The estuarine environment has a lower species diversity than either the adjacent marine or freshwater environments. However, estuaries are very productive systems and abundance can be greater than either freshwater or marine systems. The distribution of estuarine organisms is largely determined by physiological limitations in the presence of variable salinity and nutrient gradients. Thus, proceeding seaward from the freshwater environment, a progressive decrease in species occurs, with the same occurring as one proceeds upstream from the marine environment.

The estuarine environment has large detritivore populations, made up of both deposit and filter feeders as a consequence of the high productivity and the continual input of nutrients from both the freshwater and marine environments. This detritivore dominance results in relatively constant productivity in comparison to lakes or rivers which undergo seasonal maxima and minima (i.e., blooms). In addition to the primary producers, the detritivores provide a base upon which the estuarine consumers feed. Because estuarine invertebrates, especially molluscs, concentrate heavy metals, they are regarded as excellent indicators of heavy metal pollution in their environment (Phillips and Rainbow, 1988). Filter feeders may be especially useful in this regard because their microphagic nutrition and respiratory requirements necessitate the daily filtering of large volumes of water. Uptake of metals from food particles is particularly important in estuaries because major biological energy flows involve consumption of detrital particles which can have high metals content (Luoma, 1983). The food webs of the estuarine system are generally quite simple due to the low species diversity of estuarine water and sediments as discussed above. Metal uptake by detritus consumers is an important link between metal contamination and ecosystem health.

5.5 Estuarine Pollution

Whereas open oceans may generally not be polluted, the coastal waters of the sea and especially the waters of estuaries are widely polluted (McLusky, 1989). The distribution of trace metals in estuaries is controlled mainly by the distribution and transport of suspended particulate matter, especially the position of the estuarine turbidity maximum (McLusky, 1989). As a result, metal flux varies temporally along with SPM. Metal concentrations generally decrease seaward due to mixing of river borne particulates of high metal concentration with material of marine origin of relatively low metal content (Turner et al., 1991).

6.0 SYNTHESIS: METALS, DS, SPM, AND ORGANISMS

The importance of sediment geochemistry to the environmental association, behaviour, fate, and bioavailability in aquatic systems has emerged over the last decade. It is clear that suspended and deposited sediments are distinct components of the aquatic environment. As early as the mid-1970s, studies were engaged in determining the ways in which heavy metal transport was associated with suspended particle flux (DeGroot and Allersma, 1975; DeGroot 1976). Shortly thereafter, selective extractions were developed, first to examine fluvial transmission of metal contaminants (Forstner, 1978); then to specifically study the relation between metal partitioning and bioavailability (Tessier et al., 1979). Since then, selective extractions have been used in many biological studies.

However, the two have never been merged. Metal partitioning in both SPM and DS in relation to metal uptake in organisms that ingest SPM and/or DS has not been considered. As a result, there is a gap in understanding uptake pathways in particle consuming organisms. SPM:

1. plays a significant role in the transport and fate of metals in aquatic systems;
2. has the capacity to alter the speciation and hence geochemical behaviour of metals through surface complexation and biogeochemical uptake mechanisms (Douglas et al., 1993);
3. can contain higher concentrations of trace metals than bottom sediments (Juracic et al., 1986; Van Alsenoy et al., 1993; Sondi et al., 1994; Regnier and Wollast, 1995); and
4. has variable metal concentrations with maxima often found when SPM concentrations are at a seasonal low (Baeyens et al., 1987).

SPM should therefore be carefully considered in the geochemical assessment of aquatic systems, separate from analyses of deposited sediment. Ongley et al. (1982) point out that it is unlikely that bed samples adequately reflect the geochemistry of suspended matter and little is known of the qualitative changes through time either within runoff events or over the longer seasonal time frame. In order to adequately understand the biological significance of metals in aquatic systems, different pathways involved and the influence of geochemistry on bioavailability must be considered.

7.0 OBJECTIVES

The objective of this research is to further the understanding of geochemical differences between SPM and DS and the implications thereof. Specific goals (Figure 1.2) include:

1. Characterize the physico-chemical properties at three sites in the Fraser River Estuary;

2. Characterize the geochemical properties of SPM and DS at three sites in the Fraser River Estuary;

3. Determine how metals are distributed among the SPM and DS and their distributions among different binding phases in these two substrates;

4. Determine how metal concentrations are affected by temporal changes in physico-chemical and geochemical characteristics in the Fraser River Estuary;

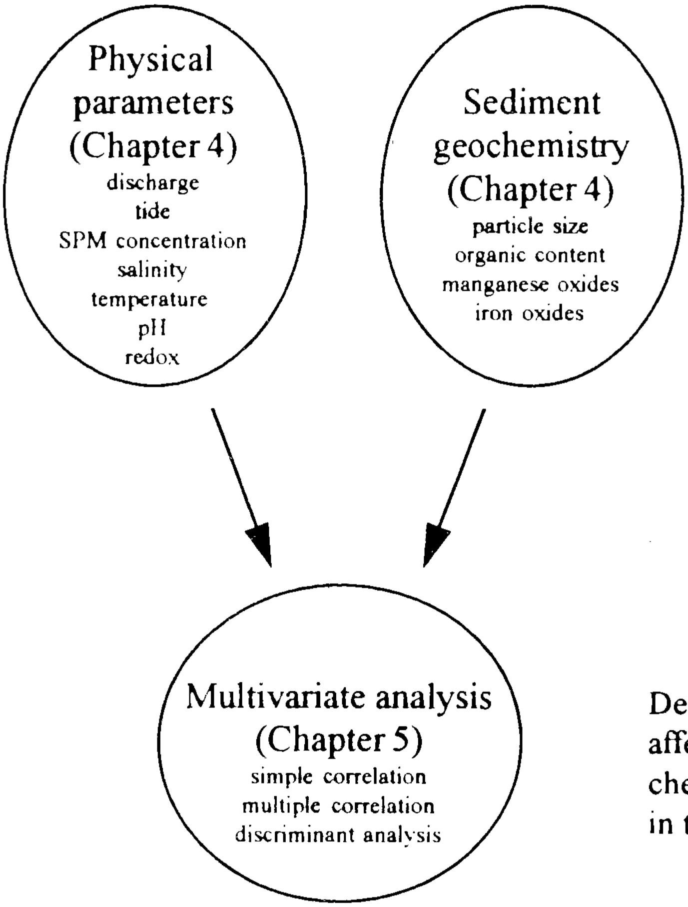
5. Determine how the geochemical characteristics of SPM versus DS affect particulate metal (^{109}Cd) assimilation efficiency in estuarine particle consumers; and

6. Determine the relative importance of SPM and DS as potential vectors of metal uptake to bivalves.

Figure 1.2 Summary of study objectives

COMPONENT

GOALS

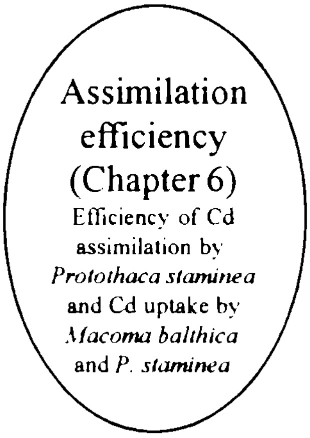


A) Characterize the physico-chemical properties at three sites in the Fraser River Estuary

B) Characterize the geochemical properties of SPM and DS in the Fraser River Estuary

C) Determine how metals are distributed among SPM and DS and their distributions among different binding phases in these two substrates

Determine how metal concentrations are affected by temporal changes in physico-chemical and geochemical characteristics in the Fraser River Estuary



A) Determine how the geochemical characteristics of SPM versus DS affect particulate metal (^{109}Cd) assimilability in estuarine particle consumers

B) Determine the relative importance of SPM and DS as potential vectors of metal uptake to bivalves

8.0 REFERENCES

Adams, W.J., R.A. Kimerle and J.W. Barnett Jr.. 1992. Sediment quality and aquatic life assessment. Environ. Sci. Technol. 26(10): 1864-1875.

Astruc, M.. 1989. Chemical speciation of trace metals. In: A. Boudou and F. Ribeyre (Eds.). Aquatic Ecotoxicology: Fundamental Concepts and Methodologies Volume I. CRC Press, Boca Raton. pp. 97-106.

Baeyens, W., G. Gillain, G. Decadt, and I. Elskens. 1987. Trace metals in the eastern part of the North Sea. 1. Analysis and short term distributions. Oceanol. Acta 10: 169-179.

Belzile, N., P. Lecomte and A. Tessier. 1989. Testing readsorption of trace elements during partial chemical extractions of bottom sediments. Environ. Sci. Technol. 23: 1015-1020.

Bendell-Young, L.I. and H.H.. Harvey. 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochim.. Cosmochim. Acta. 56: 1175- 1186.

Bendell-Young, L.I. and H.H. Harvey. 1991a. Metal concentrations in crayfish tissues in relation to lake pH and metal concentrations in water and sediments. Can. J. Zool. 69: 1076-1082.

Bendell-Young, L.I. and H.H. Harvey. 1991b. Metal concentrations in chironomids in relation to the geochemical characteristics of surficial sediments. Arch. Environ. Contam. Toxicol. 21: 202-211.

Bendell-Young, L.I., J. Chouinard and F.R. Pick. 1994. Metal concentrations in chironomids in relation to peatland geochemistry. Arch. Environ. Contam. Toxicol. 27: 186-194.

Bendell-Young, L.I., M. Dutton and F.R. Pick. 1992. Contrasting two methods for determining trace metal partitioning in oxidized lake sediments. Biogeochemistry 17: 205-219.

Boicourt, W.C.. 1993. Estuaries: Where the river meets the sea. Oceanus, Summer, 1993: 29-37.

Bourg, A.C.M. 1989. Adsorption of trace inorganic and organic contaminants by solid particulate matter. In: Aquatic Ecotoxicology: Fundamental Concepts and Methodologies, Volume I. A. Boudou and F. Ribeyre (Eds.). CRC Press, Boca Raton. pp. 107- 124.

Boyle, E.A., J.M. Redmond and E.R. Sholkovitz. 1977. The mechanism of iron removal in estuaries. Geochim. Cosmochim. Acta. 41: 1313-1324.

Bryan, G.W. 1976. Heavy metal contamination in the sea. In: Marine Pollution. R. Johnston (Ed.), Academic Press, London. pp. 185-302.

Bryan, G.W. and W.J. Langston. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Env. Poll. 76: 89-131.

Burban, P.-Y., W. Lick and J. Lick. 1989. The flocculation of fine-grained sediments in estuarine waters. J. Geophys. Res. 94(C9): 8323-8330.

Burrus, D., R.L. Thomas, J. Dominik and J.-P. Vernet. 1989. Recovery and concentration of suspended solids in the upper Rhone River by continuous flow centrifugation. Hydrological Processes 3: 65-74.

Calmano, W., J. Hong and U. Forstner. 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Wat. Sci. Tech. 28(8-9): 223-235.

Campbell, P.G.C. and A. Tessier. 1996. Ecotoxicology of metals in the aquatic environment: Geochemical aspects. In: Ecotoxicology: A hierarchical treatment. Lewis Publsihers, Boca Raton.

Campbell, P.G.C. and A. Tessier. 1989. Geochemistry and bioavailability of trace metals in sediments. In: Aquatic Ecotoxicology: Fundamental Concepts and Methodologies, Volume I. A. Boudou and F. Ribeyre (Eds.). CRC Press, Boca Raton. pp.125-148.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, A.A. Crowder, W.K. Fletcher, B. Imber, S.N. Luoma, P.M. Stokes and M. Winfrey. 1988. Biologically available metals in sediments. National Research Council of Canada Associate Committee on Scientific Criteria for Environmental Quality. NRCC No. 27694.

DeGroot, A.. 1976. Heavy metals in the Dutch Delta. In: Interactions between sediments and freshwater. H.L. Golterman (Ed.). Junk and Pudoc, The Hague. pp 104-107.

DeGroot, A. and E. Allersma. 1975. Field observations on the transport of heavy metals in sediments. Adv. Water Technol. 7: 855-895.

Dorcey, A.J. and J.R. Griggs. 1991. Water in the sustainable development: Exploring our common future in the Fraser River Basin. Westwater Research Centre, Faculty of Graduate Studies, University of British Columbia.

Douglas, G.B., R. Beckett and B.T. Hart. 1993. Fractionation and concentration of suspended particulate matter in natural waters. Hydrological Processes 7: 177-191.

Duinker, J.C., R. Wollast and G. Billen. 1979. Manganese in the Rhine and Scheldt estuaries, Part 2: Geochemical cycling. Est. Coast Mar. Sci. 9: 727-738.

Environment Canada. 1992. A state of the environment synposis: The lower Fraser River basin. Environment Canada. 11pp.

Evans, D.W., N.H. Cutshall, F.A. Cross and D.A. Wolfe. 1977. Manganese cycling in the Newport Estuary, North Carolina. Est. Coast. Mar. Sci. 5: 71-80.

Forstner, U.. 1993. Metal speciation - General concepts and applications. Intern. J. Environ. Anal. Chem. 51: 5-23.

Forstner, U.. 1978. Sources and sediment associations of heavy metals in polluted coastal regions. in: The Origin and Distribution of the Elements. L.H. Ahrens (Ed). Pergammon Press, Oxford.

Forstner, U. and G. Wittman. 1981. Metal pollution in the aquatic environment, 2nd revised edition. Springer Verlag, New York.

Foster, I.D.L. and S.M. Charlesworth. 1996. Heavy metals in the hydrological cycle: trends and explanation. Hydrol. Process. 10: 227-261.

GESAMP. 1987. Land/sea boundary flux of contaminants: Contributions from rivers. IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint group of experts on the scientific aspects of marine pollution. Reports and studies of GESAMP No. 32.

Gobeil, C., B. Sundby and N. Silverberg. 1981. Factors influencing particulate matter geochemistry in the St. Lawrence Estuary turbidity maximum. Mar. Chem. 10: 123-140.

Hart, B.T.. 1982. Uptake of trace metals by sediments and suspended particulates: A review. Hydrobiologia 188/189: 397-402.

Harvey, R.W. and S.N. Luoma. 1985a. Separation of solute and particulate vectors of heavy metal uptake in controlled suspension feeding experiments with *Macoma balthica*. Hydrobiologia 121: 97-102.

Harvey, R.W. and S.N. Luoma. 1985b. Effect of adherent bacteria and bacterial extracellular polymers upon assimilation by *Macoma balthica* of sediment bound Cd, Zn, and Ag. Mar. Ecol. Prog. Ser. 22: 281-289.

Honeyman, B.D. and P.H. Santschi. 1988. Metals in aquatic systems: predicting their scavenging residence times from laboratory data remains a challenge. Environ. Sci. Technol. 22(8): 862-871.

Hoos, L.M. and G.A. Packman. 1974. The Fraser River Estuary: Status of environmental knowledge to 1974. Report of the Estuary Working Group, Department of Environment, Regional Board Pacific Region. Special Estuary Series No. 1.

Horowitz, A.J.. 1991. A primer on sediment-trace element chemistry. 2nd Ed. Lewis Publishers Inc. 136 pp.

Horowitz, A.J.. 1986. Comparison of methods for the concentration of suspended sediment in river water for subsequent chemical analysis. Environ. Sci. Technol. 20(2): 155-160.

Horowitz, A.J., F.A. Rinella, P. Lamothe, T.L. Miller, T.K. Edwards, R.L. Roche and D.A. Rickert. 1990. Variations in suspended sediment and associated trace element concentrations in selected riverine cross sections. Environ. Sci. Technol. 24: 1313-1320.

Horowitz, A.J., K.A. Elrick and R.C. Hooper. 1989. A comparison of instrumental dewatering methods for the separation and concentration of suspended sediment for subsequent trace metal analysis. Hydrological Processes 2: 163-184.

Johnston, R. (Ed.). 1976. Marine Pollution. Academic Press, London.

Juracic, M., L.M. Vitturi, S. Rabbitti anf G. Rampazzo. 1986. Suspended matter properties and their role in pollutant transfer from river to sea. Case Study: Adige River - Adriatic Sea. Sci. Tot. Env. 55: 243-249

Kennett, K. and M.W. McPhee. 1988. The Fraser River estuary: An overview of changing conditions. Fraser River Estuary Management Program. September 1988. 31 pp.

Ketchum, B.H.. 1980. Marine industrial pollution. In: Oceanography: the past. M. Sears and D. Merriman (Eds.). Springer-Verlag, New York.

Kheboian, C. and C.F. Bauer. 1987. Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. Anal. Chem. 59: 1417-1423.

Luoma, S.N.. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci. Tot. Env. 28: 1-22.

Luoma, S.N. and E.A. Jenne. 1977. The availability of sediment bound cobalt, silver, and zinc to a deposit feeding clam. In: Biological implications of metals in the environment. R.E. Wildung and H. Drucker (Eds.). Technical Information Center, Energy Research and Development Administration, Washington, D.C., pp. 213-230.

Luoma, S.N. and E.A. Jenne. 1976. Factors affecting the availability of sediment-bound cadmium to the estuarine deposit feeding clam, *Macoma balthica*. In. Radioecology and energy resources. E. Cushing (Ed.). Dowden, Hutchinson and Ross, Stroudsburg. pp. 213-230.

Luoma, S.N., C. Johns, N.S. Fischer, N.A. Steinberg, R.S. Oremland and J. R. Reinfelder. 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. Environ. Sci. Technol. 26: 485-491.

Mantoura, R.F.C.. 1987. Organic films at the halocline. Nature: 328: 579-580.

McLusky, D.S.. 1989. The estuarine esosystem. 2nd Edition. Tertiary Level Biology. Chapman and Hall, New York. 215 pp.

Meybeck, M. and R. Helmer. 1989. The quality of rivers: from pristine stage to global pollution. Paleogeog. Paleoclimat. Paleoecol. 75: 283-309.

Milliman, J.D.. 1980. Sedimentation in the Fraser River and it's Estuary, Southwestern British Columbia (Canada). Estuar. Coastal Mar. Sci. 10: 609-633.

Millward, G.E., G.A. Glegg and A.W. Morris. 1992. Zn and Cu removal kinetics in estuarine waters. Estuar. Coast. Shelf. Sci. 35: 37-54.

Moore, R.M., J.D. Burton, P.J. LeB. Williams and M.L. Young. 1979. The behaviour of dissolved organic material, iron and manganese in estuarine mixing. Geochim. Cosmochim. Acta. 43: 919-926.

Morris, A.W.. 1985. Estuarine chemistry and general survey strategy. In: Practical estuarine chemistry: A handbook. P.C. Head (Ed.). Cambridge University Press, Cambridge. 337 pp.

Morris, A.W., A.J. Bale and R. J.M. Howland. 1982. The dynamics of estuarine manganese cycling. Estuar. Coast Shelf Sci. 14: 175-192.

Morris A.W., R.F.C. Mantoura, A.J. Bale and R.J.M. Howland. 1978. Very low salinity regions of estuaries: important sites for chemical and biological reactions. Nature 274: 678-680.

Nirel, P.M.V. and F.M.M. Morel. 1990. Pitfalls of sequential extractions. Water Research 24(8): 1055-1056.

Northcote, T.G. and P.A. Larkin. 1989. The Fraser River: a major salmonine production system. In: D.P. Dodge (Ed.) Proceedings of the International Large River Symposium. Canadian Special Publication in Fisheries and Aquatic Science 106: 172-214.

Nriagu, J.O.. 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338: 47-49.

Nriagu, J.O. and C.I. Davidson. 1986. Toxic metals in the atmosphere. Wiley Ser. Adv. Environ. Sci. Technol. 17. Wiley, New York.

Ongley E.D. and D.P. Blachford. 1982. Application of continuous flow centrifugation to contaminant analysis of suspended sediment in fluvial systems. Environ. Technol. Lett. 3: 219-228.

Ongley, E.D., B.G. Krishnappan, I.G. Droppo, S.S. Rao and R.J. Maguire. 1992. Cohesive sediment transport: emerging issues for toxic chemical management. Hydrobiologia 235.236: 177-187.

Ongley, E.D., D.A. Birkholz, J.H. Carey and M.R. Samioloff. 1988. Is water a relevant sampling medium for toxic chemicals? An alternative environmental sensing strategy. J. Environ. Qual. 17(3): 391-401.

Ongley, E.D., M.C. Bynoe and J.B. Percival. 1982. Physical and geochemical characteristics of suspended solids, Wilton Creek, Ontario. Hydrobiolgica 91: 41-57.

Phillips, D.J.H. and P.S. Rainbow. 1988. Barnacles and mussels as biomonitors of trace elements: a comparative study. Mar. Ecol. Prog. Ser. 49: 83.

Pritchard, D.W.. 1967. What is an estuary: A physical viewpoint. in Estuaries, Lauff, G.H. (Ed.). American Association for the Advancement of Science. Publication No. 83: 3-5.

Rainbow, P.S., D.J.H. Phillips and M.H. DePledge. 1990. The significance of trace metal concentrations in marine invertebrates: A need for laboratory investigation of accumulation strategies. Mar.. Poll. Bull. 21(7): 321-324.

Rao, S.S., B.J. Dutka and C.M. Taylor. 1993. Ecotoxicological implications of fluvial suspended particulates. In: Particulate matter and aquatic contaminants. S.S. Rao (Ed.). Lewis Publishers, Boca Raton pp. 157-167.

Regnier, P. and R. Wollast. 1995. Distribution of trace metals in suspended matter of the Scheldt estuary. Mar. Chem. 43: 3-19.

Rendell, P.S., G.E. Batley and A.J. Cameron. 1980. Adsorption as a control of metal concentrations in sediment extracts. Environ. Sci. Technol. 14(3): 314-318.

Sholkovitz, E.R.. 1979. Chemical and physical processes controlling the chemical composition of suspended material in the River Tay estuary. Estuarine Coastal Mar. Sci. 8: 523-545.

Sholkovitz, E.R., E.A. Boyle and N.B. Price. 1978. The removal of dissolved humic acids and iron during estuarine mixing. Earth Plan. Sci. Lett. 40: 130-136.

Sondi, I., M. Juracic, E. Prohic and V. Pravdic. 1994. Particulates and the environmental capacity for trace metals. A small river as a model for a land-sea transfer system: the Rasa River estuary. Sci. Tot. Env. 155 173-185.

Tack, F.M.G. and M.G. Verloo. 1995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. Intern. J. Environ. Anal. Chem. 59: 225-238.

Tarr, J.A. and R.V. Ayres. 1990. The Hudson-Raritan river basin. In: B.L. Turner, W.C. Clark, R.W. Kates, J.F. Richards, J.T. Mathews and W.B. Meyer (Eds.). The earth as transformed by human action. Cambridge University Press, Cambridge. pp. 623-641.

Tessier, A. and P.G.C. Campbell. 1987. Partitioning of trace metals in sediment: Relationships with bioavailability. Hydrobiologia 149: 43-52.

Tessier, A. and P.G.C. Campbell. 1988. Comments on the testing of the accuracy of an extraction procedure for the speciation of particulate trace metals in sediments. Anal. Chem. 60: 1475-1476.

Tessier, A., J. Buffle and P.G.C. Campbell. 1994. Uptake of trace metals by aquatic organisms. In: Chemical and Biological Regulation of Aquatic Systems. J. Buffle and R.R. De Vitre (Eds.). CRC Press, Boca Raton. pp. 197-230.

Tessier, A., P.G.C. Campbell, J.C. Auclair and M. Bisson. 1984. Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc *Elliptio complanata* in a mining area. Can J. Fish. Aquat. Sci. 41: 1463-1472.

Tessier, A., P.G.C. Campbell and J.C. Auclair. 1983. Relationships between trace metal partitioning in sediments and their bioaccumulation in freshwater pelecypods. In. Proceedings of the 4th International Conference on Heavy Metals in the Environment. CEP Consultants, Edinburgh, U.K.. pp. 1086-1089.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7): 844-851.

Turner. A. and G.E. Millward. 1994. Partitioning of trace metals in a macrotidal estuary: Implications for contaminant transport models. Estuar. Coast. Shelf. Sci. 39: 45-58.

Turner, A., G.E. Millward and A.W. Morris. 1991. Particulate metals in five major North Sea estuaries. Estuar. Coast. Shelf. Sci. 32: 325-346.

Van Alsenoy, V., P. Bernard and R. Van Grieken. 1993. Elemental concentrations and heavy metal pollution in sediments and suspended matter from the Belgian North Sea and Scheldt estuary. Sci. Tot. Env. 133: 153-181.

Warren, L.A. 1994. Trace metal complexation by suspended particulates in an urban river. Ph.D. Thesis, Department of Zoology, University of Toronto. 165 pp.

Warren, L.A. and A.P. Zimmerman. 1994. The importance of surface area in metal sorption by oxides and organic matter in a hetrogeneous natural sediment. Applied Geochemistry 9: 245-254.

Wollast, R.. 1982. Methodology of research on micropollutants - heavy metals. Water Sci. Technol. 14: 107-125.

Wood, J.M.. 1974. Biological cycles for toxic elements in the environment. Science 183: 1049.

CHAPTER 2: REVIEW OF GEOCHEMISTRY AND BIOAVAILABILITY

The introduction emphasized the importance of geochemistry on both the environmental behaviour and fate of metals and their interactions with aquatic biota. This review summarizes the physical and chemical features of sediments, collectively referred to as geochemistry, that the reader should be familiar with. It also presents the concept of bioavailability, the processes involved, and the role of geochemistry in influencing bioavailability.

1.0 GEOCHEMISTRY (OF THE AQUATIC PARTICLE)

Geochemistry is the study of the physical, chemical, and geological features of sediment and it's surroundings that determine the chemical state and association of a metal in the environment. The distribution of a metal among various dissolved and particulate phases is termed partitioning. Metal partitioning is a dynamic process, subject to influence by the physico-chemical environment (Luoma and Bryan, 1981). Metals may be partitioned among several forms simultaneously; the dominant form of any metal may differ substantially among chemically different sediments or within sediments over time (Luoma and Bryan, 1981). Transfer of metals from the environment to the biota is, in part, geochemistry-dependent and can be modified by many additional factors.

In the aquatic environment, free metal is rapidly adsorbed or complexed to particulate matter under normal physico-chemical conditions (Jenne and Zachara, 1987; Honeyman and Santschi, 1988; Kramer, 1988; Bourg, 1989; Warren and Zimmerman, 1994a, 1994b; Turner and Millward, 1994) and this feature is the dominant control over metal speciation. Speciation is defined as the distribution of (metal) species in solution and on solids resulting from surface:solute, solvent:solute, and solute:solute interactions (Westall, 1987). Metals can be associated with a variety of dissolved or particulate ligands (Buffle and Altmann, 1987). A ligand is any anion or molecule containing free electron pairs that can form a coordination compound (complex) with a metal cation. Due to a variety of complex physical, chemical, and biological processes, a major fraction of the trace metals introduced into the aquatic environment are found associated with sediments, distributed among a variety of physico-chemical forms (Tessier and Campbell, 1987).

Ligands in the aquatic environment are present on particle surfaces and in the dissolved form. On or in particles, they are frequently termed "geochemical phases". Surface functional groups of geochemical phases are the key constituents determining the ability of particles to form surface complexes. These groups include -OH groups (oxides), -SH (sulphides), -S-S (pyrite), -CO_2OH (carbonates) on mineral particles as well as -NH_2 and -SH groups on biological or organic surfaces (Stumm et al., 1994). The -OH surface groups are generally believed to be most important in aquatic surface complexation reactions. In the aquatic environment, ligands are often heterogeneous, polyfunctional entities displaying a variety of surface groups. Of course, properties of different metals are also important and stem from differences in outer shell electron configuration and size.

The accumulation of sediment bound metals by benthic invertebrates has been shown to be dependent upon the distribution of the trace metals among various geochemical components (Luoma, 1986). Some geochemical components of the sediments "bind" metals much more tightly than others. Tessier and Campbell (1987) note that trace metals can be:

- adsorbed at particle surfaces (e.g., clays, humic acids, metal oxides [could change with ionic composition]);
- carbonate bound (e.g., discrete carbonate minerals co-precipitated with major carbonate phases [could change with pH variation]);
- occluded in iron and/or manganese oxyhydroxides (e.g., discrete nodules, cement between particles, coatings on particles [could change with redox changes]);
- bound up with organic matter in either living or detrital form (could be released under oxidizing conditions);
- sulphide bound (e.g., amorphous sulphides formed in-situ [could be released by oxidation] or crystalline forms); and
- matrix bound (e.g., bound in lattice positions as aluminosilicates, in resistant oxides or sulphides [rarely released]).

The order of this list is reflective of the strength of geochemical association between metal and component.

1.1 Particle Properties

Aquatic particles are either suspended in the water column or deposited at the bottom and can be living or dead biotic material or abiotic material. Sedimentary particles are heterogeneous and extremely diverse, with many different components with different complexing capacities. Properties such as particle size, organic content, and metal oxide content vary among sediments and can determine the amount of metal that can be scavenged by sediment. In addition, sediments contain large bacterial populations which can sorb or take up metals (Inniss and Mayfield, 1978). This is particularly true of suspended particles, which are generally richer in organic content and have significant bacterial populations (Rao et al., 1993). Diagenesis, the chemical, physical, and mineralogical changes occurring in sediment (i.e., compaction, formation of Mn and Fe oxides, dissolution of silica, and the degradation of organic matter) (Tessier et al., 1994a), occur both in the water column and in the sediments, resulting in the progressive breakup and modification of particulates. Due to this, and to different compositional influences, suspended particulates and bottom sediment can have very different properties.

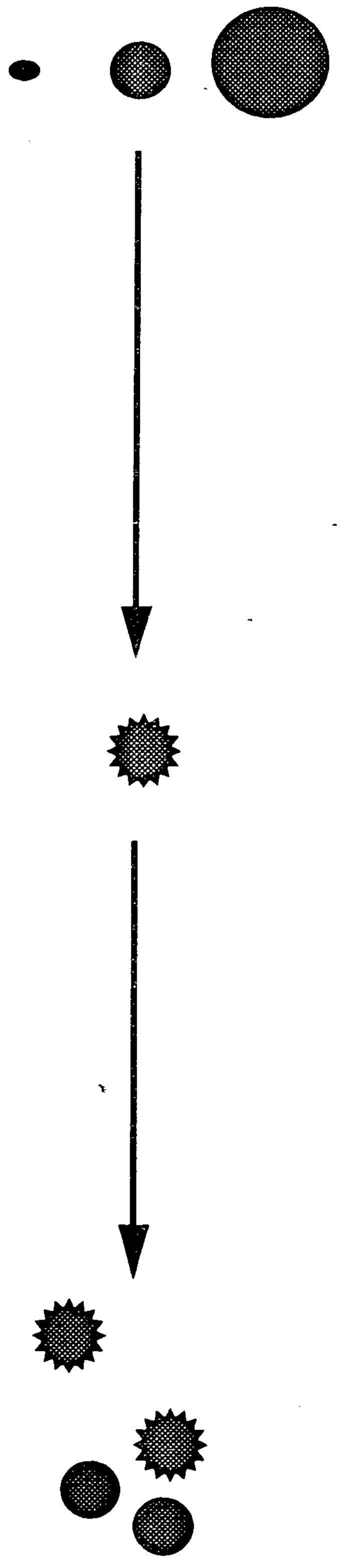
Natural waters and their particulates are characterized by their complexity and diversity. Particles include organisms, biological debris, organic macromolecules, clays, various minerals, and oxides. They can be partially coated with organic matter, oxides, and other solutes (Stumm et al., 1994). Estuarine particulate materials can be classified as lithogenous, hydrogenous, and biogenous. This classification scheme also applies to deposited sediments since they have accumulated by settling processes. Lithogenous particles are inorganic and are derived from erosive weathering of crustal material (Morris, 1985). Lithogenous material can be divided into an unreactive detrital phase (the bulk crystalline structure) and a reactive phase comprised of sorbed constituents which are subject to exchange and transfer reactions with their ambient environment (Morris, 1985). Hydrogenous material is generated within the aquatic phase and may occur as a coating on lithogenous particles or as a discrete phase. Iron and other hydrous metal oxide precipitates and humic aggregates are typical in-situ products (Morris, 1985). Biogenic particles include living biota (especially bacteria and plankton), their decaying remains, and fecal pellets (Morris, 1985). Particles in the aquatic environment exist in a variety of stages of genesis and diagenesis. Figure 2.1 summarizes the processes occurring on sediment particles in aquatic systems.

Particulates in natural waters have a continuous size distribution and include organic colloids, inorganic colloids, and submicron particles not retained by membrane filters (Stumm et al., 1994). Indeed, a significant portion of both organic and inorganic material, especially iron and manganese oxides, sulphur, and sulphides can be present as sub-micron particles (Stumm et al., 1994). Colloids are components that have the physico-chemical properties of solids but are not separated from the solution phase and are therefore operationally defined as solute (Morel and Gshwend, 1987). This arbitrary division is a weakness in deriving sorption theory, and is probably the major reason for discrepancy between experiment and theory. Douglas et al. (1993) showed that the < 0.45 μm fraction contains a range of colloidal species of diverse geochemistry, supporting the weakness of this arbitrary division. Such treatment results in artificially lower solid:solution partitioning ratios, as removal of colloids (Benoit et al., 1994) has shown. Processes of flocculation and coagulation in natural waters can rapidly change particle size distributions.

1.1.1 Particle Size

Particle size distribution, through it's control of total available surface area is a fundamental controlling factor in metal sorption. More sorptive sites are available the greater the surface area and net negative charges of particulates result in sorption of the metal cations (Morris, 1985; Horowitz and Elrick, 1987; Warren and Zimmerman, 1994a). Thus small particles, although representing small percentages of total weight, can represent large proportions of total surface area. Indeed, trace metal reactions occur predominantly at the particle surface involving surface layers of Fe oxides and organic matter (Warren, 1994). The surface area of small particulates, including iron oxides (Dzombak and Morel, 1990) and manganese oxides (Sigg, 1987) can be very large. However, the contribution of surface area and surface coatings of organic and metal oxide surface coatings to trace metal sorption can be difficult to distinguish since surface coatings may increase or decrease

Figure 2.1 Characteristics and processes of aquatic particles



Particle size

Chemical makeup of lithogenic particles
silicates, sulphides, sulphates, oxides

Chemical makeup of hydrogenic particles
surface sorption of materials present in the aquatic environment
iron oxides
manganese oxides
organic matter

Interactions between hydrogenic particle and prevailing chemical and biological conditions
increased sorption with increasing ionic strength
dissociation of oxides and proton competition at low pH
dissolution of oxides with decreasing '-' pE
dissolution of sulphides with increasing '+' pE

Interactions between hydrogenic particle and physical conditions
transport
deposition and resuspension

Interactions between hydrogenic particle and system biology
diagenesis
incorporation into biota
biological clearing

surface area, and each coating has different sorptive capacities (Horowitz and Elrick, 1987; Warren and Zimmerman, 1994a).

1.1.2 Organic Matter

Organic matter has long been recognized as an important parameter in determining metal speciation (and hence availability in aquatic systems) (Hart, 1982; Sposito, 1987). In the aquatic environment, organic matter exists in both dissolved and particulate forms, and is classified as humic or non-humic material. Non-humic material is easily recognizable as having a biogenic origin (i.e., carbohydrates, proteins, fatty acids) and is very labile and therefore present in small amounts in the aquatic environment. Humic materials are refractory materials of biogenic origin with higher molecular weight and are generally amorphous, composed of a complex mixture of hydrophillic and aromatic material (Schnitzer, 1991). Humic substances originate from the chemical and biological degradation of plant and animal residues and the synthetic activities of microorganisms (Sposito, 1987).

Metals have an affinity for organic material and form metal-organic complexes through the process of adsorption (which is any process whereby the partitioning of an ion between solution and solid phases occurs) due to surface charge. Not all organic material is reactive, some is present as aluminosilicate and carbonate coatings, parts of which are isolated from the aqueous phase. Hence rather than total organic carbon (TOC), Jenne and Zachara (1987) suggest that particulate organic carbon is the important component of particulate organic matter. Lion et al. (1982) have shown that organic coatings can strongly influence adsorption and exchange processes at particle surfaces. However, the opposite is sometimes found when organic material blankets particle surfaces or oxide surfaces without providing binding sites (Hart, 1982). The extent of organic complexation varies from close to 100% for Cu(II) in surface waters to negligible for Mn(II) and Cd, with Zn intermediate (Hering and Morel, 1990).

In many aquatic systems, a majority of metal complexation can be attributed to metal interactions with humic substances (Hering and Morel, 1990). Evidence suggests that humic acids are extremely important in complexing copper (Mantoura et al., 1978; Bendell-Young et al., 1994), but less so for other metals. The importance of these humic acids is greater in waters of low ionic strength, with the exception of copper which associates very strongly with humic acids (Mantoura et al., 1978).

1.1.3 Bacteria

Bacteria, and to a lesser extent, phytoplankton are integral components of the suspended particulate matter of fluvial and estuarine systems. Dead, decaying biota with their bacterial complement provide a major source of organic material for sorption reactions. Cell walls of bacteria and algae, and extracellular secretions of these organisms have been shown to have an overall electronegative charge and therefore have high metal binding capacities (Beveridge et al., 1993). Many researchers point out that insufficient attention has been paid to the role of bacteria in trace metal dynamics of aquatic systems (Sunda et al., 1983; Wangersky, 1986; Beveridge et al., 1993) and current knowledge is therefore weak. Regardless of the relative infancy of this area of investigation, it is clear that bacteria are important in solid-solution interface reactions which control metal behaviour in aquatic systems.

Bacteria play a dual role with respect to SPM and metal cycling in aquatic systems. In addition to their presence as a sorptive surface, they promote aggregation by adhesion as they feed on organic matter in various stages of decomposition. They also affect sediment geochemistry through their role in degrading organic material and their influence over redox conditions. Rao et al. (1993) believe that bacteria are essential for the formation and stabilization of suspended particulates and that bacteria play a key role in the adsorption and eventual transport of contaminants in fluvial systems. These authors discount the importance of geochemical factors in solid-solution partitioning of trace metals, stating that bacteria and their influence are of more importance. While these authors provide no convincing evidence to support their contention, other researchers have shown the importance of bacteria in metal geochemistry. It is clear that bacteria are important and must be considered along with geochemical phase partitioning.

Recent work has shed some light on some of the ways bacteria can influence solid-solution metal partitioning. Leppard (1993) notes that high concentrations of metals accumulate in flocs rich in extracellular polymeric substances, especially fibrils composed largely of acid polysaccharides (exuded by bacteria). Bacteria and other organisms can also decrease free metal by sorption to biogenic material released (exuded) by the organism (i.e., Morris, 1985; Stumm et al., 1994). There is evidence that bacteria can oxidize Mn(II) to Mn(IV), forming manganese oxides and manganate minerals (Mandernack et al., 1994). Further, Sunda and Kieber (1994) have found that when bacteria oxidize Mn(II), they deposit the oxide on their surfaces. Among the many reasons proposed for this, they hypothesize that Mn oxides lyse (oxidize) humic substances (to form low molecular weight organic compounds), allowing the bacteria to utilize the otherwise unavailable carbon pool in humic substances. Given the current theory that points to the importance of manganese oxides as trace metal sorption surfaces in aquatic systems, this interaction could be very important.

1.1.4 Metal Oxides

Iron, manganese, aluminum, and silicon oxides are important ligands in the aquatic environment, providing sorption sites for metals (Singh and Subramanian, 1985). The bulk of research on the influence of metal oxides in the aquatic environment has focussed upon the oxides of Mn and Fe; since particles dominated by iron (III) (hydr)oxides and manganese (III,IV) (hydr)oxides are found in many natural water and soil systems (Stumm et al., 1994), and along with organic matter have been shown to be the most important substances for metal sorption (Jenne and Zachara, 1987). Iron oxides are predominantly present as FeOOH (iron oxyhydroxide), $Fe(OH)_3(H_2O)_3$ (hydrous iron hydroxide), and Fe_2O_3 (iron oxide); manganese oxides are present as MnO_2 (manganese oxide) and MnOOH (manganese oxyhydroxide) (Singh and Subramanian, 1985; Stumm and Morgan, 1996). The reactive groups of the metal oxides are the surface water or hydroxyl groups, which provide binding sites for free metal ions (Stumm and Morgan, 1996). Oxides of Fe exist in layers on particle surfaces or as mineralogic Fe. The crystallinity of the Fe oxides varies over a continuum from highly amorphous (diffuse) to highly crystalline (Luoma and Bryan, 1981). Surface area of these oxides can be very large per unit weight.

Hydrous oxides of Mn and Fe are important geochemical components determining the speciation of metals (Lion et al., 1982; Tessier et al., 1985; Bendell-Young and Harvey, 1991, 1992). Bendell-

Young and Harvey (1991, 1992) note that the three most important geochemical components in sediments include oxides of Mn and Fe (along with organic matter). Manganese oxides are more easily reducible than are iron oxides, therefore, metals sorbed to manganese oxides are less strongly associated than with iron oxides. This has important implications for redistribution and release. Decreased pH causes protonation of surface groups and can lead to dissolution of metal oxides, a reaction which is enhanced by light and reducing conditions (Stumm and Furrer, 1987). The recent increase in the use of manganese in gas additives has the potential to influence the aquatic behaviour of other metals due to its effect on the total quantity of manganese oxides.

1.2 Physico-Chemical Variables

Physico-chemical factors of greatest significance at the geochemical level include:

- salinity (ionic strength)
- pH (proton concentration)
- Eh (electron concentration)
- temperature
- total ligand and types

1.2.1 Salinity

In estuarine and marine systems, trace metal adsorption has been shown to decrease with increasing salinity (Bourg, 1987). Higher ionic strength results in more competition for the available ligand binding sites and hence relatively more free (dissolved) metal. Salinity can also induce flocculation (aggregation of particles) in estuaries with high organic content. This will decrease total available surface area and act as a net metal removal process as the larger particles settle. Overall, pronounced removal of trace constituents (to bottom sediments) can occur in an estuary's turbidity maximum (Sholkovitz et al., 1978; Gobeil et al., 1981; Turner et al., 1993; Turner and Millward, 1994). Increasing salinity can result in complexation of some metals (particularly Cd and Zn) with anions such as chloride (Turner et al., 1981; Mantoura, 1987; Turner and Millward, 1994) thereby keeping more metal in the dissolved state. Chloride complexes on particle surfaces can decrease a particle's sorptive capacity for metals. The base cations (most importantly Na^+, Ca^{2+}, and Mg^{2+}) are the major ion competitors encountered as salinity rises.

1.2.2 pH (proton concentration)

The acidity (pH) of a water body is one of the key variables determining metal speciation, due to it's controlling influence on both solid and solution phase surface charges (Warren, 1994). The dependency of adsorption on pH reflects solution hydrolysis or protonation of the adsorbing ions, and more importantly, the surface charge properties of the adsorbent (Jenne and Zachara, 1987) (i.e., protonation of -OH groups).

In circum-neutral systems, particles are negatively charged and attract metal ions; however, as pH drops, particles lose their negative charge, attracting ligands rather than metal ions (Stumm et al., 1994). Metal complexes with both organic and inorganic ligands tend to dissociate as pH decreases, resulting in increased free ion concentration (Campbell and Stokes, 1985). This occurs due to reverse hydrolysis favouring the aquo ion, and H^+ competition for ligands (protonation of binding sites) (Campbell and Stokes, 1985). The result is an increase in the proportion of free metal ion. Indeed, some researchers have noted release of metals from sediments upon rapid acidification (Schindler, 1987; Tessier et al., 1994a).

1.2.3 Eh (oxidation-reduction potential)

Eh, the electron concentration of a matrix, is a measure of it's reducing or oxidative capacity, and as such determines the state in which a metal will be present. Changing redox conditions can affect metals by changing the oxidative state of the metal ion or by changing the availability of binding sites on competing ligands or chelates (Jenne and Zachara, 1987; Warren, 1994). This includes formation (oxidation) and dissolution (reduction) of metal oxides. In aquatic systems, metal oxides are important oxidants, while biogenic organic particles, metal sulphides, and Fe(II) bearing minerals are important reductants (Stumm et al., 1994).

Under reducing conditions, metals are often present bound to sulphides in their most reduced state. Although anoxic sediments are generally of little concern in terms of metal exposure to benthic organisms (Campbell and Tessier, 1989), they can be important in metal cycling. Under reducing conditions, most metals become quite insoluble and are fixed in the reduced sediment as metal sulphides. Manganese and iron become more soluble and dissolve into the pore waters, returning to the oxic layer by diffusion, where they are oxidized and form precipitates (Waldichuk, 1985).

1.2.4 Temperature

Temperature can influence the partitioning of metals in aquatic systems. Warren (1994) found that a decrease in temperature (from 10 °C to 1 °C) decreased partitioning to the particulate phase. Other researchers, working at higher temperatures have noted an increase in partitioning to the particulate phase with increasing temperature (Byrne et al., 1988; Johnson, 1990).

Sorption is an endothermic reaction, absorbing heat from it's surroundings (positive ΔH). Hence, increased temperatures will favour sorption, while at low temperatures the reverse holds. In addition, decreased kinetic energy at lower temperatures will cause the sorption reaction to occur more slowly. Increased temperature will also result in increased bacterial growth and enhanced bacterial sorption.

1.2.5 Total Ligands

The rates of complexation reactions in natural waters will depend on the initial speciation of both metals and ligands, the relative concentrations of reacting species, the strength of metal-ligand interactions, and the ligand structure (particularly the extent of metal-ligand binding) (Hering and Morel, 1990). Ligands vary greatly in both their properties and their complexity; the most important ligand in terms of metal sorption being suspended particles. In the pH range of natural waters, most particles carry a negative charge (Stumm et al., 1994).

The concentrations and types of ligands influence free metal concentrations through simple Michaelis-Menten first order kinetics, where intrinsic properties of the metal-ligand association (strong or weak binding [Km]) and the concentrations of metal and ligand determine the association velocity (v). In general, the higher the concentration or binding strength of ligand, the lower the concentration of free metal. Apparent binding constants depend somewhat on the ratio of metal bound per surface area, since binding constants become weaker as the strongest binding sites become limited (Stumm et al., 1994; Botelho, 1994). The hardness cations Ca^{2+} and Mg^{2+} are important because they bind with ligands thus competing with some metals (i.e., Paalman, 1994), notably the first transition series metals (Jenne and Zachara, 1987). However, Jenne and Zachara (1987) also note that the major cations are not effective competitors for trace metal sorption sites since these sites possess considerable selectivity. For example Ca^{2+} and Mg^{2+} inhibition is frequently observed for Zn but not for Cd or Cu (Luoma, 1983). For Cu, this stems from it's exceptional binding capacity with organic ligands (Luoma, 1983). Such competition (and differences therein) is especially important in high ionic strength solutions such as occur in estuarine and marine environments.

A variety of types of metal associations with ligands are possible. For example, natural organics, such as dissolved organic carbon (MW range 10^3 - 10^5) form soluble and insoluble complexes with trace metals. Metal oxides are very important ligands in natural waters. Chloro-complexes are particularly important for cadmium (up to 84%; Mantoura et al., 1978, 1987). The reactivity of particles depends upon the type of surface species present. These groups include -OH groups (oxides), -SH (sulphides), -S-S (pyrite), $-CO_2OH$ (carbonates) on mineral particles as well as $-NH_2$ and -SH groups on biological or organic surfaces (Stumm et al., 1994).

1.2.6 Interactions

Interactions can occur between any of the factors presented above. Of particular importance in the metal interactions with particles and biota in the aquatic environment is the interrelation between particle size, organic matter content, iron oxide content, and manganese oxide content. Warren and Zimmerman (1994a, 1994b) found that particle size and the particle's complement of organic matter and iron oxide were the most important factors governing trace metal particulate interactions. They note that the relative importance of the surface phases varies from metal to metal. Chemical influence over such interrelationships is also important. For example, Bendell-Young and Harvey (1992) showed a major interaction between pH and the way metals partition among oxide and organic phases in lake sediments.

2.0 BIOAVAILABILITY

The "availability" of metals to aquatic organisms is intimately linked to the geochemical (matrix and physical) factors previously discussed. Uptake of sediment bound metals by benthic invertebrates has been shown to be dependent on their distribution among the various geochemical components (Luoma, 1986); total metal concentrations are inadequate for determining the fate and biological significance of metals in aquatic systems. Not only do geochemical factors influence the environmental association, behaviour, and fate of metals; they also influence biotic uptake. Whether uptake occurs as dissolved metal or from a component of a heterogeneous particle, the combination of geochemistry and biology must be considered. Differences between metal uptake to a fish or clam (or any other aquatic organism) will be a product of differences in the interplay of biological factors with geochemical factors. Although the biological significance of trace metals is complex and is still poorly understood (Tessier and Campbell, 1987; Rainbow et al., 1990), anthropogenic alteration of aquatic systems is such that toxicity is a concern; all trace metals are potentially toxic at a threshold bioavailability (Rainbow et al., 1990).

2.1 Exposure and Uptake: Bioavailability

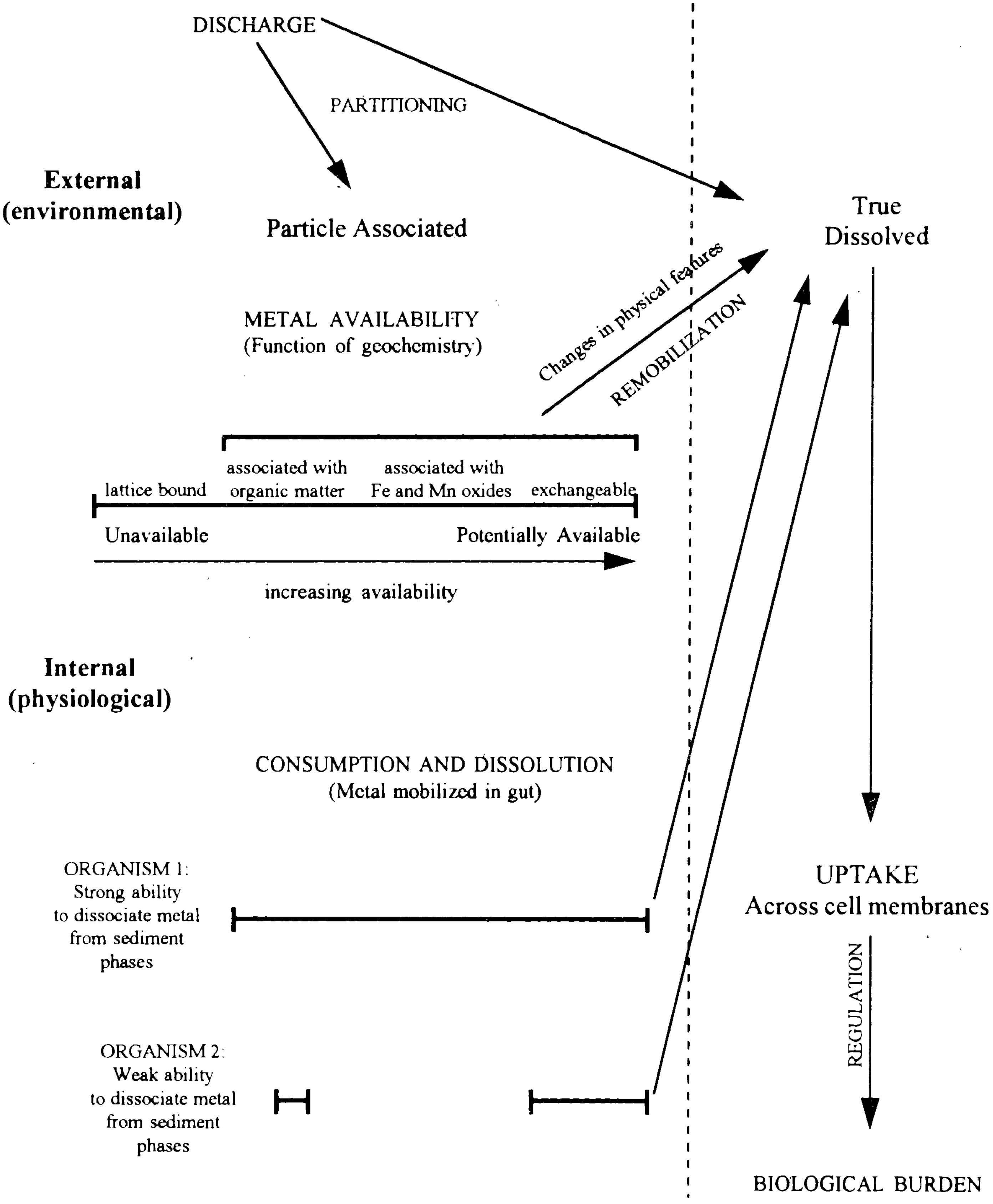
Bioavailability is a product of exposure and uptake, and is a commonly used descriptor of the importance or "threat" represented by a metal in the environment. Both elements of bioavailability should be considered. Campbell et al. (1988) consider a metal to be in a biologically available chemical state when it can be taken up by the organism and can react with it's metabolic machinery. Bioavailability must also consider metal that can be released or redistributed by physical (i.e., pH or redox) or biological (i.e., digestion) changes. Here, **bioavailability is strictly taken to encompass exposure and uptake, being an estimate of the capacity of a metal to end up in an organism, regardless of whether it subsequently reacts with metabolic machinery**. A conceptual diagram of bioavailability is provided in Figure 2.2. Estimates of bioavailability are critical to an appreciation of the potential of metals to exert biological effects.

2.1.1 Exposure

Organisms come into contact with metals in many forms. It is intuitively clear that for uptake to occur, an organism and a contaminant must make contact. Thus, exposure is relative to the organism of interest but is also a result of geochemical processes that determine the form and distribution of a metal (Figure 2.2). For benthic invertebrates, especially deposit or filter feeders, exposure to either dissolved or particulate forms can occur. Exposure is linked to the amount of free or releasable metal in the immediate vicinity of the organism (for metals, geochemistry-dependent) and to an organism's physiological and behavioral characteristics.

Many factors influence exposure, including physical factors (flow, currents, etc.) resulting in the spatial distribution of metal; chemical factors (pH, redox, etc); geochemical factors (particle load, matrix properties) that influence association and distribution; and the location and habits of organisms. Physico-chemical and geochemical factors can vary over different scales, controlling the spatial and temporal distribution of metals. Biological factors determine the spatial and temporal distribution of organisms. For benthic sediment ingesters, it is generally acknowledged that oxidized sediments of aquatic systems are of most relevance (Luoma and Davis, 1983). Benthos are exposed to particles from an oxic environment either because they live above the anoxic zone or because they have siphons or tubes extending to the oxic zones of the sediments (i.e., they can create their own oxic microenvironments) (Campbell and Tessier, 1989). Behavioral factors are also important, such as where an organism chooses to live and how it feeds. Invertebrates can filter suspended material for food, ingest sediment with some selectivity based on particle size or density, where others are

Figure 2.2 Relationship between factors influencing metal bioavailability



indiscriminate sediment ingesters (Tessier et al., 1994b). Also, as metal is strongly associated with organic material, it is believed that organisms maximize their exposure by seeking high quality food (Luoma, 1989; 1990).

2.1.2 Uptake

Uptake is a biological process which can be measured experimentally. As such, it is an endpoint that can be used to develop an understanding of how geochemical factors (which can be manipulated) affect the subset of total metal taken up by organisms. It is useful to consider uptake as a two step process, the first step involves the metal entering the body of an organism, the second entering a cell.

Bodily uptake, separated from exposure is simply the amount of contaminant that is internalized via any route. Sediment-ingesting organisms can take up both free and particulate metals (Tessier et al., 1994b). Due to the high concentrations of metals in the sediment relative to the water column, uptake of even a small fraction of the total sediment assumes considerable importance, especially in filter feeding and burrowing organisms that consume sediment (Bryan and Langston, 1992). Thus, significant differences in metal uptake can exist between suspension and deposit feeders exposed in the same metal enriched system (Luoma, 1989). In addition, the bodily compartment that is exposed (gut, gill, skin) is important, although uptake of ingested sediment is the focus of this work.

Metal uptake in aquatic organisms is proportional to free metal exposure. For organisms that feed on (or accidentally ingest) sediments, uptake is also proportional to metal concentration in the food, feeding rate, and assimilation efficiency (Bruggeman, 1988). However, food is most often an intermediary, with very few exceptions metal must be released to the free form to be transported across biological membranes. In the gut, metal uptake is a function of quantity and quality (or type) of food ingested, the geochemistry of the ingested material, and digestive properties of the organism. The weaker the association between the metals and the particles ingested, the easier uptake occurs. Digestive processes are an important consideration for organisms that consume metal-containing material, since ingested materials are subjected to acid and enzymatic extraction (or basic extraction in the case of some polychaetes) in the gut (Luoma, 1983). Relatively little is known about digestive processes in invertebrates and even less is known about conditions inside the digestive vesicle or amoebocytes in the many invertebrate species that employ intracellular digestion (Campbell and Tessier, 1989). It is clear however, that the stronger the gut extraction, the more metal can be potentially available. In general, only a poor correlation has so far been found between digestive pH (over the range 5-7 in filter feeders and 6-7 in deposit feeders) and metal uptake, possibly due to H^+ competition (Luoma, 1983).

Once metals are released in the gut, geochemistry still has a role to play in determining uptake. Metals freed in the digestive tract can undergo complexation reactions with ligands on the gut membrane (Luoma, 1983). However, much as competition for ligands can have an effect on how much metal is bound; so competition for uptake sites (in the gut or externally) will determine how much metal is taken up (Luoma, 1983). Metals can interfere in each others uptake or competition for metals can occur between unreacted sediment components in the gut (ligands) and gut binding sites (Campbell et al., 1988; Tessier et al., 1994b). Metals that were desorbed in the gut can be re-absorbed in the mid-gut, and eliminated through the feces. Evidence suggests that complexation of a metal with lipid soluble material or a nutrient can greatly increase uptake.

The cell membrane is the environmental interface of an organism, a non-polar lipid membrane impregnated with molecules that sequester and help transport essential polar substances across the membrane (Luoma, 1983); it is also a selective, semi-permeable barrier to transport. Metals can cross cell membranes by carrier-mediated transport, by transport through protein channels, by passive diffusion, and by endocytosis (Tessier et al., 1994b). Carrier mediated transport is the most important process and occurs via protein carriers. It can occur by four different mechanisms (Campbell et al., 1988): transport by carriers specific for a given metal or transport on these due to geochemical similarity; non-specific complexation of metal forms with carrier molecules; transport of metals associated with essential organic nutrients on carriers specific for the nutrient; and transport of nutritionally essential metals as complexes. The second process involves transport through protein channels that extend through a membrane, presenting hydophilic groups. The third process is passive diffusion of lipid-soluble metal forms (i.e., methyl-mercury). Lastly, endocytosis of particulates can occur in some organisms (i.e., molluscs). This occurs when membrane invagination engulfs a particle and fuses to form an intracellular vesicle. The first two processes are important for free metal ions, while processes 3 and 4 are important for particulates and metals associated with dissolved ligands (i.e., colloids). Once inside the cell, metals are rapidly bound to a range of intracellular ligands. This maintains a free ion concentration gradient.

2.1.3 Regulation

All metals are toxic at a threshold of bioavailability (Rainbow et al., 1990). While bioavailability is a prerequisite to toxicity, bioavailability cannot predict toxicity to different organisms. This is because many organisms have effective means by which internalized metal can be made biologically inert. This is termed regulation. Although regulation generally has a cost, it minimizes the impact of metals that are taken up.

Regulation strategies in invertebrates involve either temporary storage and excretion or storage detoxification (Rainbow et al., 1990). In temporary storage, metals are processed into detoxified granules, which can be excreted over time. Organisms with lower metal permeability will pick up less metal and have more time to excrete detoxified granules. Storage detoxification involves permanent storage of metal either in tissues that have low metal sensitivity or as detoxified forms. The induction of metal detoxification systems involving the formation of granules or metal binding proteins leads in some species to tissue concentrations orders of magnitude higher than normal (Bryan and Langston, 1992), often with no deleterious effects. Different mechanisms of metal storage may affect interpretation of experimental results dependent upon whole tissue analyses (Luoma, 1989), and key differences can exist for different metals, particularly for essential versus nonessential metals. For example, Zn is commonly regulated homeostatically, while Cu is less regulated and the nonessential metals Cd, and Pb are not specifically regulated (Luoma, 1983).

3.0 SUMMARY

Sediment geochemistry is important in influencing the environmental behaviour and bioavailability of sediment-associated trace metals. It also influences the concentration of free metal ions through surface complexation reactions. An improved understanding of geochemical characteristics of different sediments in relation to bioavailability is required to determine the relative importance of different sediments to sediment-ingesting organisms. The objectives outlined in chapter 1 are designed to address these needs. In association with quantifying the importance of suspended and deposited particulates as food to various organisms, relationships between assimilation and sediment geochemistry will improve prediction of metal assimilation risk in these organisms. The latter part of this requirement is addressed in the objectives of this study, as the bioavailability of ^{109}Cd is compared from the two sediment types.

4.0 REFERENCES

Bendell-Young, L.I. and H. Harvey. 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochim. Cosmochim. Acta. 56: 1175-1186.

Bendell-Young, L.I. and H.H. Harvey. 1991. Metal concentrations in chironomids in relation to the geochemical characteristics of surficial sediments. Arch. Environ. Contam. Toxicol. 21: 202-211.

Bendell-Young, L.I., J. Chouinard and F.R. Pick. 1994. Metal concentrations in chironomids in relation to peatland geochemistry. Arch. Environ. Contam. Toxicol. 27: 186-194.

Benoit, G., S.D. Oktay-Marshall, A. Cantu II, E.M. Hood, C.H. Coleman, M.O. Coracioglu and P.H. Santschi. 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids and solution in six Texas estuaries. Mar. Chem. 45: 307-336.

Beveridge, T.J., S.S. Rao, S.A. Daniels and C.M. Taylor. 1993. Suspended particle research: current approaches and future needs. In: S.S. Rao (Ed.). Particulate Matter and Aquatic Contaminants. Lewis Publishers, Boca Raton. pp.197-205.

Botelho, C.M.S., R.A.R. Bonaventura and M.L.S.S. Goncales. 1994. Interactions of lead (II) with natural river water: part I. Soluble organics. Sci. Tot. Env. 149: 69-81.

Bourg, A.C.M.. 1987. Trace metal adsorption modelling and particle-water interactions in estuarine environments. Continental Shelf Res 7: 1319-1332.

Bruggeman, W.A.. 1988. Bioaccumulation. In Manual on aquatic ecotoxicology. H.A.M. de Kruijf and D. de Zwart, Eds. Kluwer Academic Publishers, Boston. pp. 149-153.

Bryan, G.W. and W.J. Langston. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Env. Poll. 76: 89-131.

Buffle, J.. and R.S. Altmann. 1987. Interpretation of metal complexation by heterogeneous complexants. In. Aquatic Surface Chemistry. W. Stumm (Ed.). Johm Wiley and Sons, New York. pp. 351-384.

Byrne, R.H., L.R. Kump and K.J. Cantrell. 1988. The influence of temperature and pH on trace metal speciation. Mar. Chem. 25: 163-181.

Campbell, P.G.C. and A. Tessier. 1989. Geochemistry and bioavailability of trace metals in sediments. In: Aquatic Ecotoxicology: Fundamental Concepts and Methodologies Volume I. A. Boudou and F. Ribeyre (Eds.). CRC Press, Boca Raton. pp. 125- 148.

Campbell, P.G.C. and P.M. Stokes. 1985. Acidification and toxicity of metals to aquatic biota. Can. J. Fish. Aquat. Sci. 42: 2034-2049.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, A.A. Crowder, W.K. Fletcher, B. Imber, S.N. Luoma, P.M. Stokes and M. Winfrey. 1988. Biologically available metals in sediments. National Research Council of Canada Associate Committee on Scientific Criteria for Environmental Quality. NRCC No. 27694.

Douglas, G.B., R. Beckett and B.T. Hart. 1993. Fractionation and concentration of suspended particulate matter in natural waters. Hydrological Processes 7: 177-191.

Dzombak, D.A. and F.M.M. Morel. 1990. Surface complexation modelling of hydrous ferric oxide. Wiley Interscience, New York. 331 pp.

Gobeil, C., B. Sundby and N. Silverberg. 1981. Factors influencing particulate matter geochemistry in the St. Lawrence Estuary turbidity maximum. Mar. Chem. 10: 123-140.

Hart, B.T.. 1982. Uptake of trace metals by sediments and suspended particulates: A review. Hydrobiologia 188/189: 397-402.

Hering, J.G. and F.M.M. Morel. 1990. The kinetics of trace metal complexation: Implications for metal reactivity in natural waters. In. Aquatic Chemical Kinetics. W. Stumm. (Ed.). John Wiley and Sons, New York. 145-171.

Honeyman, B.D. and P.H. Santschi. 1988. Metals in aquatic systems: predicting their scavenging residence times from laboratory data remains a challenge. Environ. Sci. Technol. 22(8): 862-871.

Horowitz, A.J. and K.A. Elrick. 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Appl. Geochem. 2: 437-451.

Inniss, W.E. and C.I. Mayfield. 1978. Psychotrophic bacteria in sediments from the Great Lakes. Water Res. 12: 237.

Jenne, E.A. and J.M. Zachara. 1987. Factors influencing the sorption of metals. In. Fate and effects of sediment- bound chemicals in aquatic systems. K.L. Dickson, A.W. Maki and W.A. Brungs (Eds.). Pergammon Press, New York. pp. 83-98.

Johnson, B.B.. 1990. Effect of pH, temperature, and concentration on the adsorption of cadmium on geothite. Env. Sci. Technol. 24: 112-118.

Kramer, C.J.M.. 1988. Chemical speciation. In Manual on aquatic ecotoxicology. H.A.M. de Kruijf and D. de Zwart, Eds. Kluwer Academic Publishers, Boston. pp. 67-76.

Leppard, G.G.. 1993. Organic flocs in surface waters: their native state and aggregation behaviour in relation to contaminant dispersion. In: S.S. Rao (Ed.). Particulate Matter and Aquatic Contaminants. Lewis Publishers, Boca Raton. pp. 169-195.

Lion, L.W., R.S. Altman and J.O. Leckie. 1982. Trace metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings. Env. Sci. Technol. 16: 660-666.

Luoma, S.N.. 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Heavy metals in the marine environment. R.W. Furness and P.S. Rainbow (Eds.). CRC Press, Boca Raton.

Luoma, S.N.. 1989. Can we determine the biological availability of sediment-bound trace elements? Hydrobiol 176/177: 379-396.

Luoma, S.N.. 1986. A comparison of two methods for determining copper partitioning in oxidized sediments. Mar. Chem. 20: 45-59.

Luoma, S.N.. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci. Tot. Env. 28: 1-22.

Luoma, S.N. and J.A. Davis. 1983. Requirements for modelling trace metal partitioning in oxidized estuarine sediments. Mar. Chem. 12: 159-181.

Luoma, S.N. and G.W. Bryan. 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Sci. Tot. Env. 17: 165-196.

Mandernack, K.W., J. Post and B.M. Tebo. 1995. Manganaese mineral formation by bacterial spores of the marine Bacillus, strain SG-1: evidence for the direct oxidation of Mn(II) to Mn(IV). Geochim. Cosmochim. Acta 59(21): 4393-4408.

Mantoura, R.F.C.. 1987. Organic films at the halocline. Nature: 328: 579-580.

Mantoura, R..F.C., A. Dickson and J.P Riley. 1978. The complexation of metals with humic materials in natural waters. Estuar. Coast. Mar. Sci. 6: 387-408.

Morel, F.M.M. and P.M. Gshwend. 1987. The role of colloids in the partitioning of solutes in natural waters. In. Aquatic Surface Chemistry. W. Stumm (Ed.). Johm Wiley and Sons, New York. pp. 405-422.

Morris, A.W.. 1985. Estuarine chemistry and general survey strategy. In: Practical estuarine chemistry: A handbook. P.C. Head (Ed.). Cambridge University Press, Cambridge. 337 pp.

Rainbow, P.S., D.J.H. Phillips and M.H. DePledge. 1990. The significance of trace metal concentrations in marine invertebrates: A need for laboratory investigation of accumulation strategies. Mar.. Poll. Bull. 21(7): 321-324.

Rao, S.S., B.J. Dutka and C.M. Taylor. 1993. Ecotoxicological implications of fluvial suspended particulates. In: S.S. Rao (Ed.). Particulate Matter and Aquatic Contaminants. Lewis Publishers, Boca Raton. pp. 157-167.

Schindler, D.W.. 1987. Detecting ecosystem responses to anthropogenic stress. Can. J. Fish. Aquat. Sci. 44: 6-25.

Schnitzer, M.. 1991. Soil organic matter - the next 75 years. Soil Science 151: 41-58.

Sholkovitz, E.R., E.A. Boyle and N.B. Price. 1978. The removal of dissolved humic acids and iron during estuarine mixing. Earth Plan. Sci. Lett. 40: 130-136.

Sigg, L. 1987. Surface chemical aspects of the distribution and fate of metal ions in lakes. In. W. Stumm (Ed.) Aquatic Surface Chemistry. Wiley and Sons, New York. pp. 319-349.

Singh and Subramanian. 1984. Hydrous Fe and Mn oxides - scavengers of heavy metals in the aquatic environment. CRC Crit. Rev. Env. Control 14(1): 33-90.

Sposito, G.. 1987. Sorption of trace metals by humic materials in soils and natural waters. CRC Crit. Rev. Env. Control 16(2): 193-229.

Stumm, W. and G. Furrer. 1987. The dissolution of oxides and aluminum silicates; examples of surface-coordination-controlled kinetics. In. Aquatic Surface Chemistry. W. Stumm (Ed.). Johm Wiley and Sons, New York. pp. 197-219.

Stumm, W. and J.J. Morgan. 1996. Aquatic chemistry: Chemical equilibria and rates in natural waters. Third Edition. Wiley and Sons, New York. 1022 pp.

Stumm, W. L. Sigg and B. Sulzberger. 1994. The role of coordination at the surface of aquatic particles. In Chemical and Biological Regulation of Aquatic Systems, J. Buffle and R.R.. De Vitre (Eds.). Lewis Publishers, Boca Raton. 385 pp.

Sunda W.G. and D.J. Kieber. 1994. Oxidation of humic substances by manganese oxides yields low-molecular-weight organic substrates. Nature 367: 62-64.

Sunda, W.G., S.A. Huntsman and G.R. Harvey. 1983. Photoreduction of manganese oxides in seawater and it's geochemical and biological implications. Nature 301: 234-236.

Tessier, A. and P.G.C. Campbell. 1987. Partitioning of trace metals in sediment: Relationships with bioavailability. Hydrobiologia 149: 43-52.

Tessier, A., R. Carignan and N. Belzile. 1994a. Processes occurring at the sediment-water interface: Emphasis on trace elements. In. Chemical and Biological Regulation of Aquatic Systems. J. Buffle and R.R. De Vitre (Eds.). CRC Press, Boca Raton. pp. 137-173.

Tessier, A., J. Buffle and P.G.C. Campbell. 1994b. Uptake of trace metals by aquatic organisms. In. Chemical and Biological Regulation of Aquatic Systems. J. Buffle and R.R. De Vitre (Eds.). CRC Press, Boca Raton. pp. 197-230.

Tessier, A., F. Rapin and R. Carignan. 1985. Trace metals in oxic lake sediments: possible adsorption to iron oxyhydroxides. Geochim. Cosmochim. Acta. 49: 183-194.

Turner. A. and G.E. Millward. 1994. Partitioning of trace metals in a macrotidal estuary: Implications for contaminant transport models. Estuar. Coast. Shelf. Sci. 39: 45-58.

Turner, A., G.E. Millward, A.J. Bale and A.W. Morris. 1993. Application of the K_D concept to the study of trace metal removal and desorption during estuarine mixing. Estuar. Coast, Shelf Sci. 36: 1-13.

Turner, D.R., M. Whitfield and A.G. Dickson. 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta 45: 855-881.

Waldichuk, M.. 1985. Biological availability of metals to marine organisms. Mar. Poll. Bull. 16(1): 7-11.

Wangersky, P.J.. 1986. Biological control of trace metal residence time and speciation: A review and synthesis. Mar. Chem. 18: 269-297.

Warren, L.A. 1994. Trace metal complexation by suspended particulates in an urban river. Ph.D. Thesis, Department of Zoology, University of Toronto. 165 pp.

Warren, L.A. and A.P. Zimmerman. 1994a. The importance of surface area in metal sorption by oxides and organic matter in a heterogeneous natural sediment. Appl. Geochem. 9: 245-254.

Warren, L.A. and A.P. Zimmerman. 1994b. Suspended particulate oxides and organic matter interactions in trace metal sorption reactions in a small urban river. Biogeochemistry 23: 21-34.

Westall, J.C.. 1987. Adsorption mechanisms in aquatic surface chemistry. In Aquatic surface chemistry: Chemical processes at the particle-water interface. Stumm, W. (Ed.) Wiley and Sons, New York.

CHAPTER 3: METHODS

1.0 Study Sites

Site selection was based primarily on sediment deposition patterns, such that chosen locations were mudflats capable of supporting deposit and filter feeding organisms. The three sites incorporate sufficient distance along the estuary to provide a gradient of fluvial versus marine influence. Differences in other relevant physico-chemical factors were also expected to occur along this gradient (i.e., salinity, pH, particle size, flocculation, turbidity) with implications on metal partitioning. Sampling was undertaken at standard intervals once every month at each site by boat. Over the course of sampling (one year), this included a wide variety of conditions experienced by estuarine biota. Thus, the variability of estuarine conditions as influenced by seasonal changes in river discharge and semi-diurnally with the tidal cycle was incorporated into the study design.

All sites were at the south side of the river which is less channelized than the north side and therefore less turbulent. As a result, more deposition occurs here. Sampling locations were as follows (Figure 3.1).

1. Upstream site: northern end of Deas Island, in Gravesend Reach on the south side of the River. This is the location of a large mudflat, at the western end of which is a small bay, leading to the Ocean Cement plant. Samples were taken at the western end of the mudflat.

2. Midstream site: south side of Ladner Reach, directly opposite a flood warning tower on Kirkland Island and adjacent a bird observation tower overlooking Ladner Marsh. This site has a large mudflat; samples were taken directly opposite the Kirkland Island tower.

3. Downstream site: off the western end of Reifel Island, just south of the Albion Box. Samples were taken on a mudflat on the eastern side of a large pool.

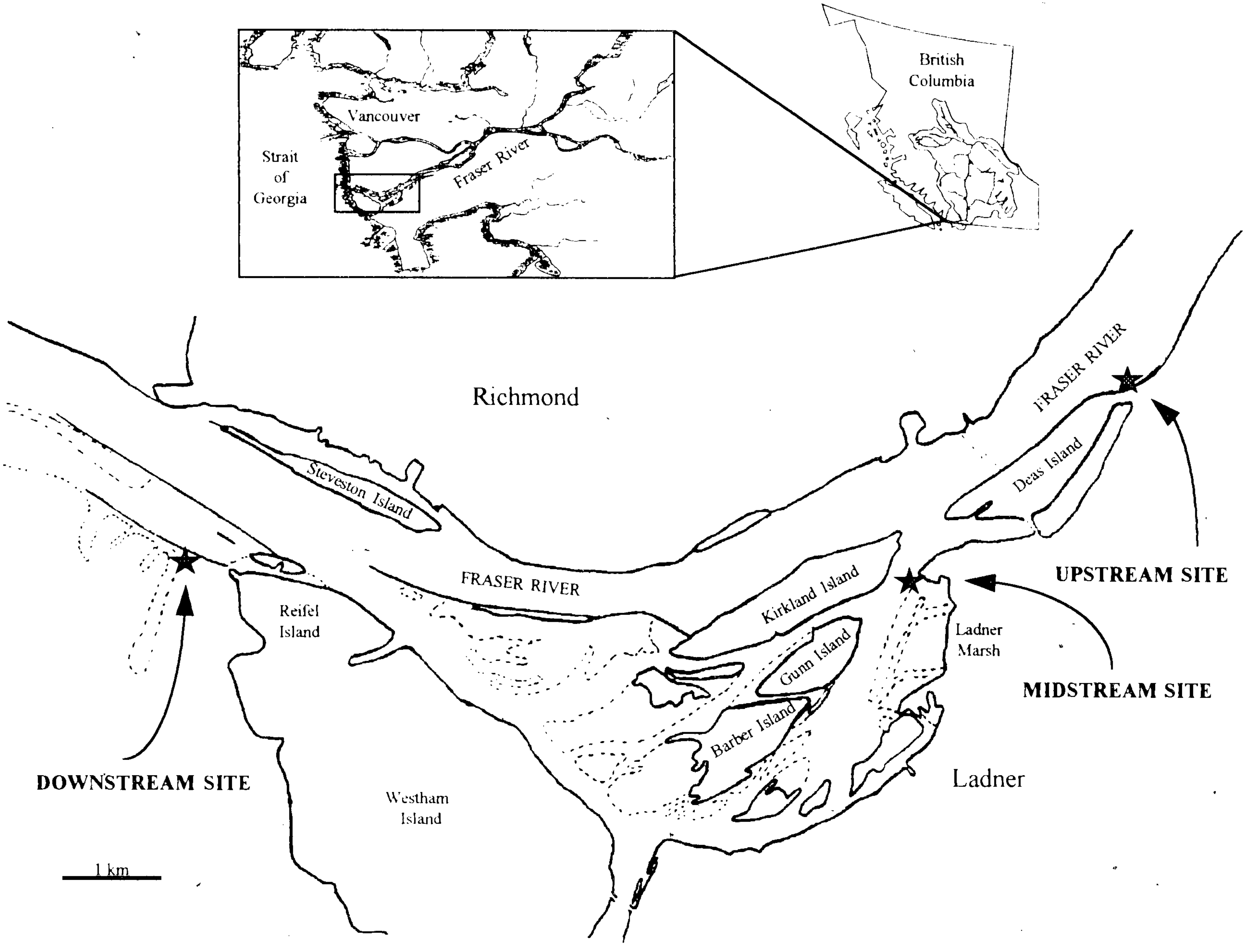


Figure 3.1 Location of sediment sampling sites

2.0 Geochemical Characterization of SPM and DS and Supportive Measures

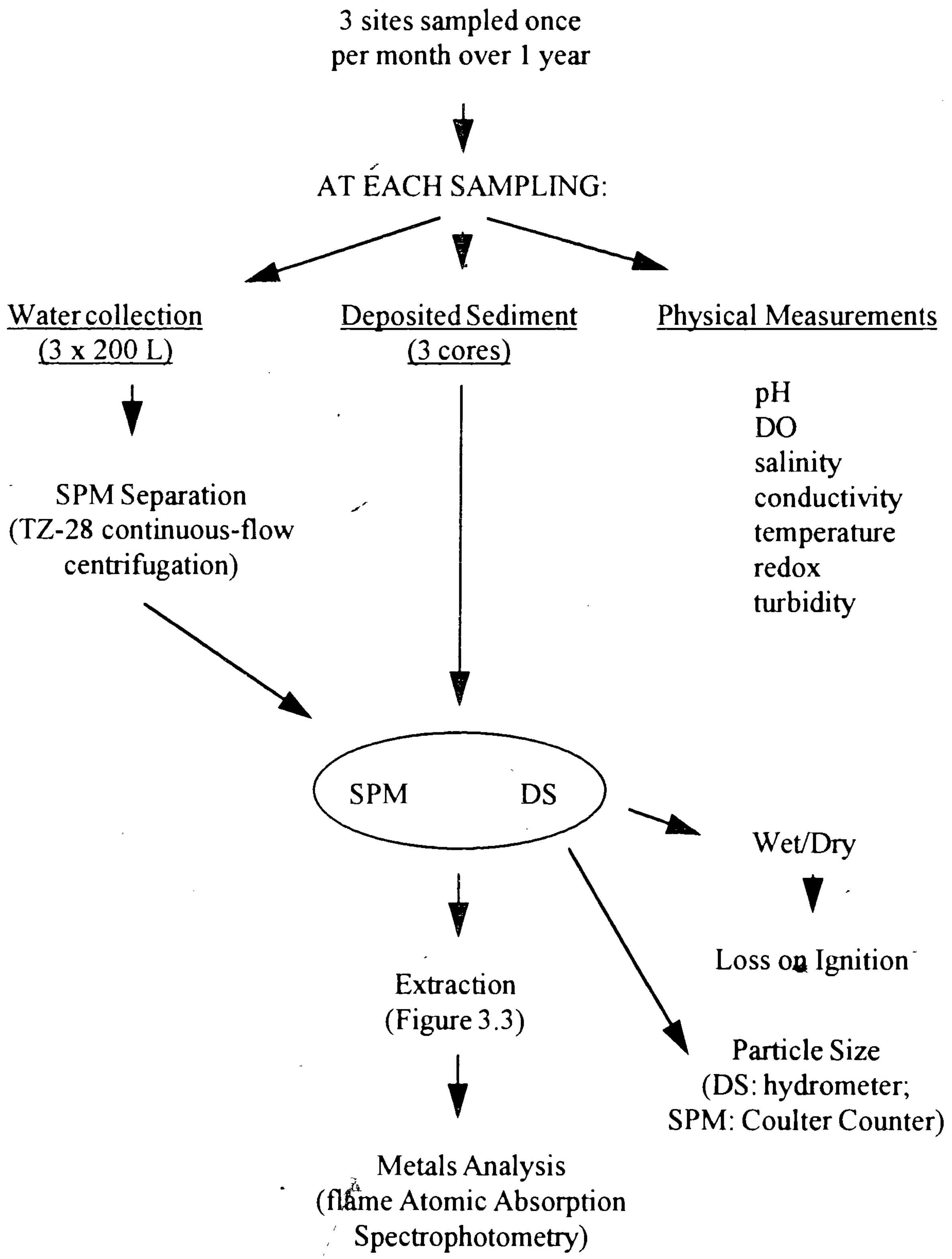
Collection, laboratory processing and analysis of Fraser River Estuary sediments was undertaken over the course of one year (August 1994 to August 1995). Additional chemical and physical parameters were assessed concurrently (Figure 3.2).

2.1 Collection

At each site, water containing suspended sediments was collected in pre-washed 20 L plastic buckets, with two field rinses according to APHA (1992). Near surface water was collected on mudflats covered by no greater than 1.5 m of water. Because the < 63 μm fraction of suspended material is not depth dependent, suspended sediment recovery for geochemical purposes can be accomplished by sampling close to the water surface (Ongley and Blachford, 1982; Horowitz et al., 1990, Ongley et al., 1992). The < 62 fraction is suspendable at any current speed while larger material is limited by the transport capacity of a given flow (Knighton, 1984). Thus, the collection of suspended particles in this manner is a good technique for collecting sediment samples for both geochemical analysis and for it's biological relevance. Three replicates of 10 buckets each (3 x 200 L) and three sediment cores (using a Wildco hand corer) were taken at each site. The oxic (surficial) portion of these cores (above the visible redox colour change) were put into acid-washed glass jars for transport to the laboratory for subsampling and analyses. The oxic portion generally varied from 2 to 8 cm depth.

Concurrent data collected during all sampling trips included turbidity, temperature, pH, dissolved oxygen, conductivity, oxidation-reduction potential, and salinity. Turbidity was measured using a turbidity test kit; all other data were recorded using a Hydrolab Surveyor II. Fraser River discharge data was kindly provided by the Water Survey of Canada (Environment Canada).

Figure 3.2 Field sampling, measurement, and sediment processing



2.2 Processing

All samples were immediately transported to the laboratory where they were kept refrigerated at 5°C until processing (always within 72 hrs). Care was always used to avoid disturbance which could result in destruction of the fragile sediments.

SPM was separated from the 200 L water samples by flow through centrifugation using the Sorvall TZ-28 system in GK continuous flow mode in a Sorvall RC5C Centrifuge. Centrifugation was done at a speed of 15,000 RPM which results in an RCF at the liquid-rotor wall interface of 24,900 and an RCF of 9200 at the water inflow point. Processing of the 200 L takes approximately 5 hours run-time at 15,000 RPM, with a flow rate of between 0.6 to 0.75 L/min. Following a run, sediment was removed from the rotor chamber using an acid-washed rubber spatula. Total sediment yields were recorded over the course of the study.

Continuous-flow centrifugation has been used by many researchers to separate SPM from natural waters (Ongley et al., 1982; Ongley and Blachford, 1982; Horowitz, 1986; Horowitz et al., 1988; Schoer, 1990; Sinclair et al., 1989; Rees et al., 1991; Warren, 1994). In a comparison of several methods for collecting estuarine SPM, Etcheber and Jouanneau (1980) note that although particles are separated by density rather than by size, continuous flow centrifugation technique is preferred (to filtration or traps) due to it's speed, high recovery rate, and reduced potential for post sampling alteration of SPM. Ongley et al. (1992) found that at a flow rate of 6 L/min, recovery efficiency was 90-95% in the fall, but fell considerably in the summer (to as low as 15%) as the organic content of the SPM rose. That is, as specific gravity of the SPM decreases, separation becomes less efficient. Overall, the dewatering efficiency of various different flow-through centrifuge systems has generally been found to be greater than 90% for incoming particles over 0.25 µm (Santiago et al., 1990).

2.3 Extractions

Once the suspended sediment samples were centrifuged, subsamples of both suspended and deposited sediment were taken for extraction. For the SPM collected by flow-through centrifugation, equally portioned 0.200 to 1.000 gram (wet wt.) subsamples were taken depending upon yield. For the three DS replicates, 1.000 gram subsamples were taken. The DS cores were maintained intact such that subsamples were composed only of the surface of the intact oxic core. All subsamples were taken with acid-washed glass stir sticks, and placed into acid-washed 50 mL centrifuge tubes. All subsamples were accurately weighed to the third decimal place using a Sartorius BA110 balance.

The samples were subjected to a simultaneous extraction procedure following the methods of Bendell-Young et al. (1992). Five sediment subsamples of approximately equal size were required. Thus, a total of 15 DS and 15 SPM subsamples per site were processed. This provided a total of 90 subsamples per month. Subsamples were divided among the treatments as outlined in Figure 3.3. The simultaneous extraction procedure of Bendell-Young et al. (1992) divides sediment into the operationally defined geochemical categories of: easily reducible (associated with the Mn oxide phase); reducible (associated with the Mn and Fe oxide phase); organic (organically bound); and aqua regia (near total digest). All subsamples were treated with a 15 to 1 ratio of analytical-grade (Baker Instra Analyzed or BDH Analar) extractant to sediment.

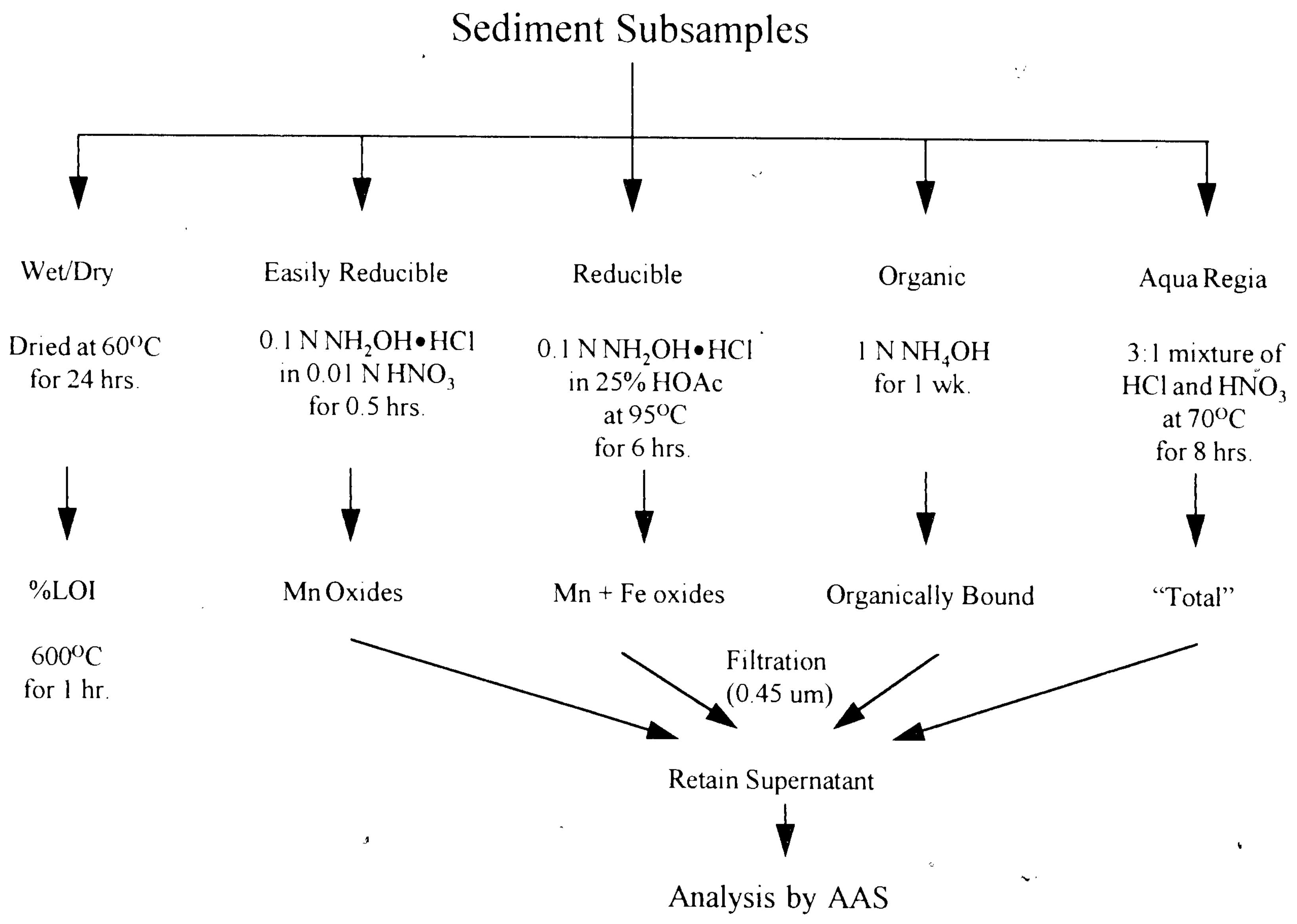
Easily Reducible

The easily reducible metals are determined by extraction with 0.1 N $NH_2OH•HCl$ in 0.01 N HNO_3 for ½ hour. This procedure extracts the easily reducible metals, those metals bound to manganese oxides (Chao, 1972) and all easily extractable components including phosphates, carbonates, and reactive iron.

Reducible

The reducible metals are determined by extraction with 0.1 N $NH_2OH•HCl$ in 25% HOAc at 95 °C for 6 hours. This procedure extracts the easily reducible metals (those metals bound to manganese oxides) <u>and</u> the reducible metals (those bound to iron oxides) (Tessier et al., 1979). The reducible metals can be determined after analysis by subtracting the easily reducible fraction from the reducible fraction. Since this procedure uses separate subsamples from sediment that has not been homogenized, it is possible to get negative concentration values in this phase.

Figure 3.3 Sediment extraction procedure



Organic

The organic metals (associated with the organic material) are determined by extraction with 1 N NH_4OH for 1 week (Luoma, 1986).

Aqua Regia

Concentrations of acid extractable metals are determined by extraction with a 3:1 ratio of HCl and HNO_3 overnight at 70 °C. This is a commonly used technique for determining the metals in sediment and is considered a near total digest of the fractions that are potentially bioavailable. More complete digestion techniques exist (i.e., HF digest), but these digest components of the sediment (i.e., crystalline minerals) that are not relevant in a biological context. Residual metal is determined as aqua regia minus the other three phases. Since this procedure uses separate subsamples from sediment that has not been homogenized, it is possible to get negative concentration values in this phase.

Extract Removal and Storage

After digestion under the appropriate conditions, the extracts (supernatants) were removed from the centrifuge tubes through Millipore Millex-HV sterilizing filter units (0.45 µm) using acid washed 10 mL syringes. This procedure ensures that no particulates are included in the extract. Extracts were stored at 5 °C in acid-washed glass or high density polyethylene (HDPE) vials for analysis.

2.4 Metal Analysis

Chemical analyses for metal in the different sediment components were carried out by flame atomic absorption spectrophotometry with the exception of cadmium, which was done by graphite furnace atomic absorption spectrophotometry (GFAAS) at the Environmental Engineering analytical laboratory at the University of British Columbia. In FAAS, a sample is aspirated into a flame and atomized; in GFAAS, a graphite furnace is used as the atomizer. A light beam is directed through the atomized sample into a monochromator, and onto a detector that measures the amount of light absorbed by atoms. Each metallic element has it's own characteristic absorption wavelength. A source lamp composed of that element is employed, minimizing spectral or radiation interferences. The amount absorbed in the flame is proportional to the concentration of the element in the sample.

Copper, iron, manganese, lead, and zinc were analyzed on a Perkin-Elmer 1100B FAAS following standard optimization procedures. Cd was analyzed on a Perkin Elmer 4100 ZL GFAAS. Samples stored at 5 °C following extraction were allowed to warm up to room temperature prior to analysis. For each metal, concentration was calculated from a calibration curve of standards plotted by the Perkin-Elmer computer. Sample concentrations were corrected for matrix quenching. Standards were made by serial dilutions of stock solutions (Sigma Chemical Company). Metals were analyzed within the linear range of the calibration curve. As required, samples were diluted (1/10, 1/50, or 1/100) to bring them into the linear range. Samples were diluted using a 1.0 mL Re-Pipet diluter; 1/50 and 1/100 dilutions were achieved by serial dilution. For quality assurance/quality control (QA/QC), NRC reference standards (MESS-2) and reagent blanks were analyzed (Appendix II). Extract concentrations of copper, iron, manganese, and zinc were generally well above detection. Extract concentrations of lead were often below the detection limits of the FAAS. In these cases, detection limits were determined as twice the background variability in the absorbance signal. This was determined in continuous mode under 20 times signal amplification. The conditions of analysis for each metal, including detection limits are provided in Appendix II.

2.5 Matrix Determinations

In addition to the chemical analyses outlined above, determinations of sediment matrix parameters were undertaken. Matrix determinations included: wet/dry weight (to standardize concentrations); particle size; loss on ignition (LOI) as a measure of organic content; iron oxide content; and manganese oxide content

Wet wt./Dry wt.

The wet weight to dry weight ratio was determined by weighing a subsample of sediment while it is wet, drying it at 60 °C to a constant weight, and weighing it again. The ratio of wet wt. to dry wt. was then calculated, and provides an indication of the porosity of the sediments. In it's final form, data is expressed as concentration per dry weight.

Particle Size Analysis

Particle size was determined by two different methods due to restrictions imposed by different methods. SPM particle size was determined using a model T_A Coulter Counter with an aperture of 100µ. A suspension of particles in 3% NaCl solution were counted for 5 seconds. Three analytical replicates of each sediment were counted. DS could not be analyzed by Coulter Counting due to problems with clogging the aperture. Attempts to switch apertures proved unfruitful.

DS particle size was determined using the hydrometer method. This method uses Stokes' Law and the observed changes in specific gravity of a solution as particles settle over time to calculate particle size. This method cannot be used with SPM, due to sample size requirements (40 g). Particle size analysis was undertaken on DS composites made from the three DS cores per site; thus 1 particle size analysis is conducted per site per sampling. The sediment samples were mixed with a dispersing agent (calgon) and put into a graduated cylinder into which a hydrometer is added. Measurements on the hydrometer are taken at standardized time intervals. These time intervals correspond to known settling velocities of different size fractions. Thus, particle percentages of sand, silt and clay are attainable.

LOI

Loss on ignition was determined by heating a sediment subsample at 600 °C for 1 hr. in a blast furnace. By weighing the sample before and after treatment, the organic and inorganic proportions were determined. LOI was performed on the dried sediment samples following calculation of wet wt./ dry wt..

Iron and Manganese Oxides

Iron oxide concentrations were determined for each sample as the concentration (mg/kg) of reducible iron (rFe). Manganese oxide concentrations were determined for each sample as the concentration (mg/kg) of easily reducible manganese (erMn).

2.6 Data Calculations and Statistical Analysis

For all sediment analyses, the metals content is expressed as mg/kg dry wt. Data from the four extractions were used to construct metal partitioning diagrams to visually assess partitioning among the leachable and residual fractions, and, where possible, among the four geochemical phases. Metal partitioning in sediments was determined by dividing the concentration of metals in each phase by the total metal recovered. Total metal recovered was generally taken as the aqua regia digest; in cases where recovery from aqua regia was lower than recovery from the three phases, the sum of metals from the three phases was used as a total value.

Statistical analyses were carried out using SAS, version 6.08 as outlined in Figure 3.4 and 3.5. Comparisons of sediment features over time, in the two sediment types, and among sites were determined using ANOVA with multiple contrasts (SAS, 1990). Tukey's multiple contrasts were used where there are three or more categories. Bonferroni t-tests were used when only two categories were present, with significance summarized as stars on the respective figures. In both cases, the experimentwise probability level was 0.05. In all analyses, proportional data was arcsine transformed and concentration data were log transformed except in the analyses where negative values were present (metal concentrations). Correlations between physical parameters and sediment features were determined (SAS, 1990).

Figure 3.4 Statistical analysis of matrix features

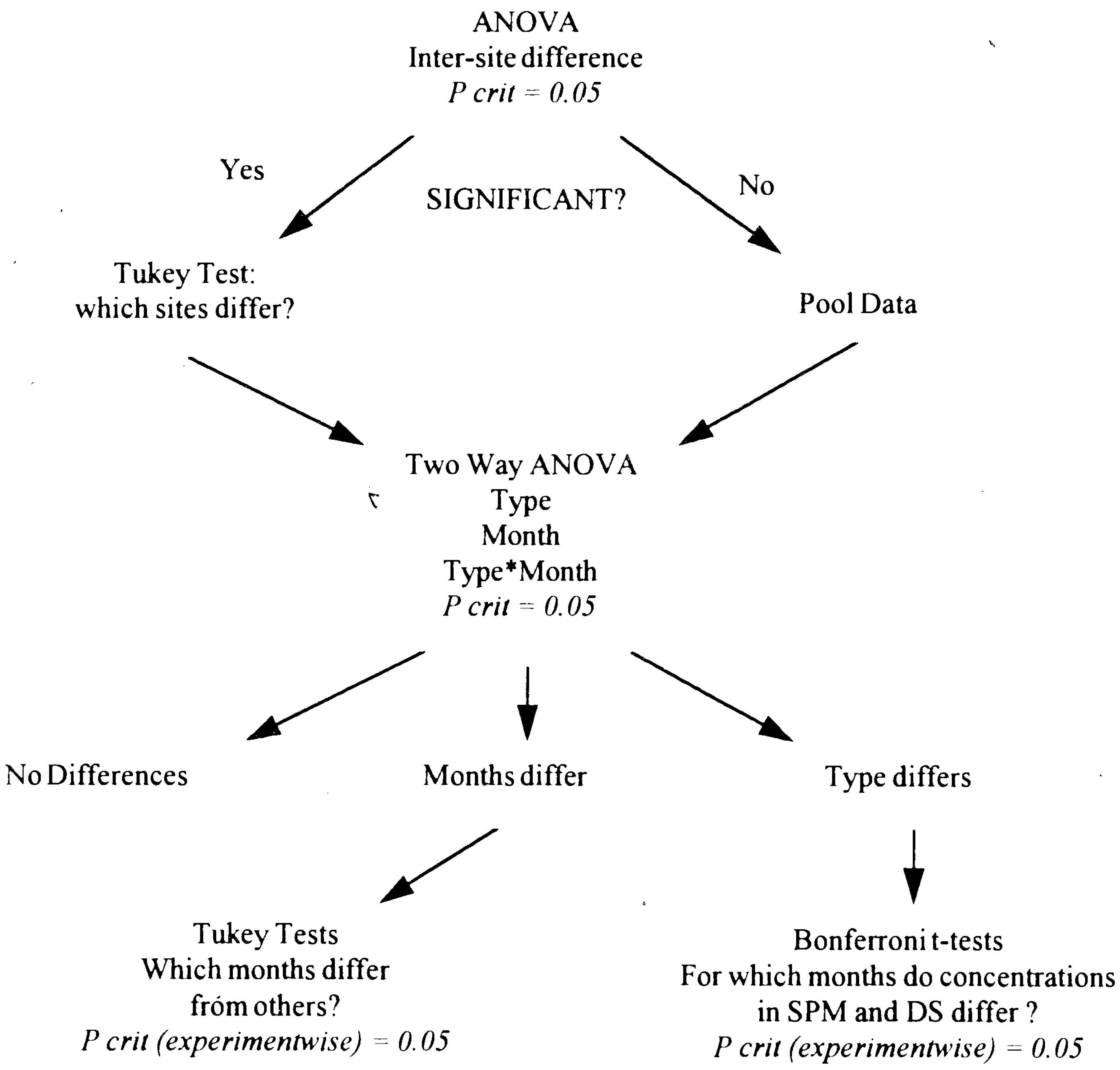
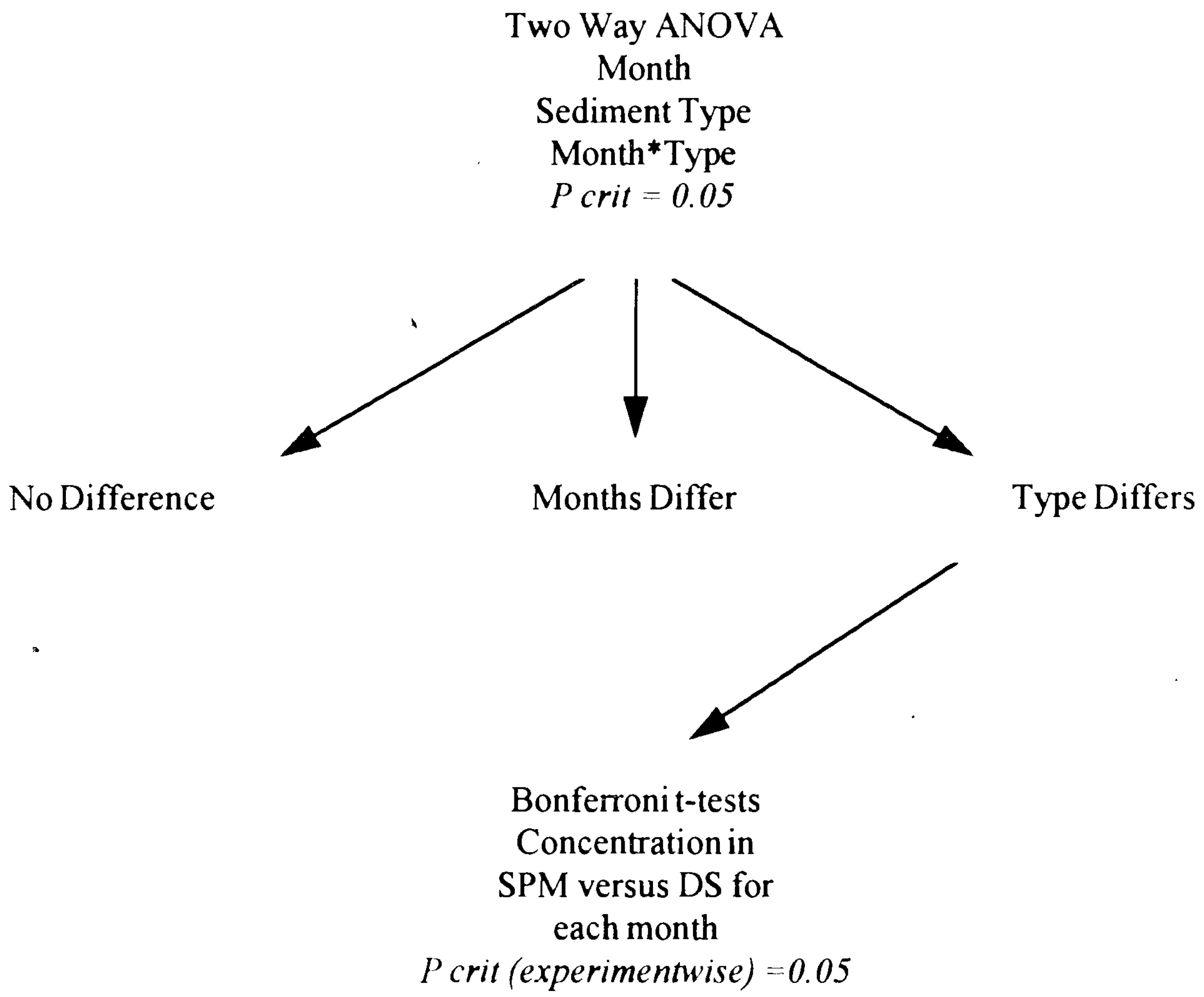


Figure 3.5 Statistical analysis of metal concentrations and partitioning



3.0 Multivariate Analyses

Relationships between the physico-chemical and geochemical features of the Fraser River Estuary and its sediments with the concentrations of metals in the sediments were assessed using multivariate statistics outlined in Figure 3.6. Simple correlations (SAS, 1990), were used to determine which of the physico-chemical and geochemical variables were significantly linearly related. In addition, simple correlations between metals concentrations and physico-chemical and geochemical factors were run. Multiple correlations (SAS, 1990) were then used to summarize the relationship between the key physico-chemical and geochemical variables and metal concentrations over the course of the study. Multiple correlation determines linear combinations of variables such that correlation with a dependent variable is maximized (SAS, 1990). Multiple correlations with the physico-chemical and geochemical variables were run for each metal in each phase. Canonical discriminant analysis was used to determine combinations of variables that best reveal seasonal differences (SAS, 1990). Given a classification variable, canonical discriminant analysis derives canonical variables that best summarize between class variation. Canonical discriminant analysis with month as a classification variable was run with all geochemical features to determine which of these best represent the variability over time.

4.0 Assimilation Experiments

Assimilation experiments were run in test aquaria with two types of sediment-dwelling clam, *Protothaca staminea* and *Macoma balthica*. Assimilation efficiency and uptake from SPM and DS were assessed for *P. staminea*, and uptake was assessed in *M. balthica*. Due to space constraints, the two experiments could not be run at the same time and were run sequentially. Both sediments were collected from the mid-estuarine site, subsamples of which were processed as outlined in section 2.2. For the SPM assimilation experiment, a total of 4000 L of water was processed to obtain sufficient SPM.

Figure 3.6 Multivariate statistical analysis

PROCEDURE	OBJECTIVE
1. Simple Correlations	determine the relationships among physico-chemical and geochemical variables
	Determine the relationships between metals and physico-chemical and geochemical variables
2. Multiple Correlations	How well do geochemical factors describe the variability of each metal over time?
	How well do physico-chemical factors describe the variability in each metal over time?
	How well do both geochemical and physico-chemical factors describe the variability of each metal over time?
3. Discriminant Analysis	What factors best describe geochemical variability over time?
	What factors best describe physico-chemical variability over time?

4.1 Field Collection

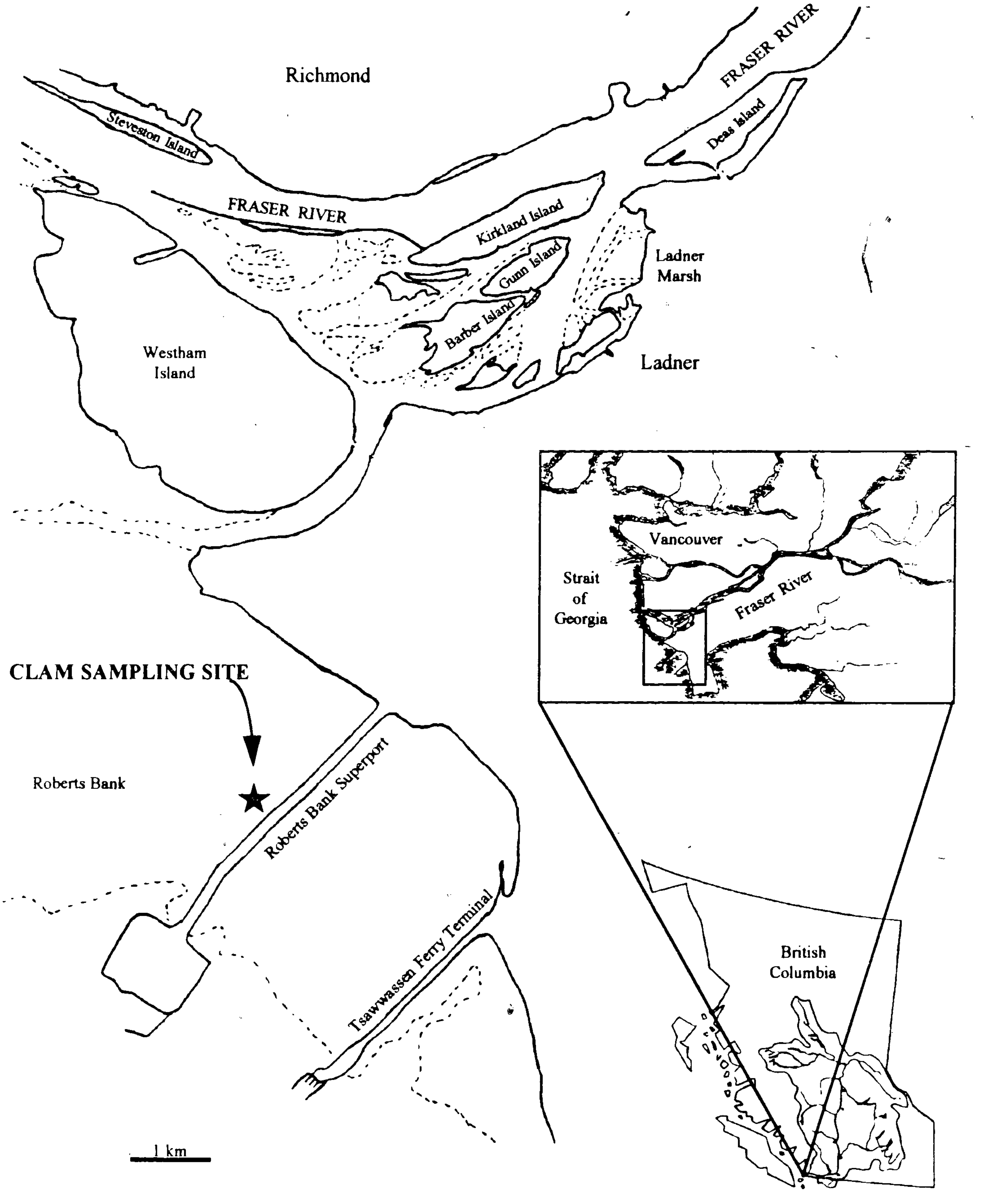
Organisms were collected in the Ladner/Tsawwassen area adjacent to the Roberts Bank jetty (Figure 3.7). This area has accessible *Protothaca staminea* and *Macoma balthica*. *P. staminea*, the common Pacific littleneck clam, was collected by raking the mudflats 100 to 200 m out from the midpoint of the jetty on the northwest side. The collected organisms ranged in size from 3.5 to 5 cm (approximately 4 to 6 years old; Fraser and Smith, 1928). *M. balthica*, the Baltic tellin, was collected by hand, by gently hand raking the sediment, feeling for the small (8 to 14 mm) clams. Organisms were stored in buckets containing seawater and were transported to the lab where they were acclimatized and depurated in a filtered seawater and filtered dechlorinated water mixture for a minimum 72 hrs before the initiation of assimilation experiments.

4.2 Sediment Spiking

To expose the clams to sediments containing the radioisotope, sediments had to first be spiked with appropriate quantities of radioisotope. Spiking for DS was done on September 28, 1995; the spikes for SPM, on December 6, 1995. The spikes for the exposures were done on an equivalent dry weight of 5.000g (8.19 grams of wet DS and 13.16 grams of wet SPM, at dry/wet ratios of 0.61 and 0.38 respectively). To each of the three HDPE bottles were added the sediment and 205 mLs of site water (25:1, DS wet). To these bottles, 2268 kBq of ^{109}Cd ($t_{1/2}$ 453 d) and 924 kBq of ^{241}Am ($t_{1/2}$ 432 y.) was added. This yielded an interim slurry of 10.84 kBq/mL ^{109}Cd and 4.51 kBq/mL ^{241}Am which was shaken every day for 12 days before being added to the exposure aquaria. In the exposure aquaria, the total isotope concentration diluted to 222 Bq/mL (2.43 ppb) ^{109}Cd, and 92 Bq/mL ^{241}Am.

To determine how the isotopes distribute within the sediments, small aliquots of sediment (1.000 g of DS and 1.605 g of SPM; equivalent dry weight) were added to centrifuge tubes, with 25 mLs of water, and spiked with the two isotopes. To these centrifuge tubes were added 27.8 kBq of ^{109}Cd and 11.5 kBq of ^{241}Am such that the concentration in the centrifuge tubes was 1112 Bq/mL (12.15 ppb) ^{109}Cd and 462 Bq/mL ^{241}Am. These slurries were set up in three categories with three replicates each, and were mixed every day and left to sit for three different time intervals (1 week, 3 weeks and

Figure 3.7 Organism collection site



7 weeks). At the end of the interval, the slurries were centrifuged, extracted by the method of Bendell-Young et al. (1992), and the extracts counted on the gamma detector.

4.3 Exposures

In the assimilation and uptake experiments, the radioisotope ^{109}Cd was used with ^{241}Am as an inert tracer in the concentrations noted above. Assimilation efficiencies and uptake characteristics were determined from the two sediment types (SPM vs. DS). Salinity was held at levels approximating levels found at the collection site (~14 ppt) and was achieved using filtered seawater and filtered dechlorinated freshwater mix. Temperature was set at 12°C.

The experimental design used three replicate 38 L aquaria with 36 *P. staminea* and 20 *M. balthica* per aquaria. Controls were run in the exposure aquaria using 0.45 µm Millipore filters as dividers (Harvey and Luoma, 1985). This allowed half the organisms to be exposed to the particulates, while the other half were exposed only to the free (dissolved) radioisotope. Eighteen *P. staminea* and 10 *M. balthica* were used on each side of the aquarium. These were sampled on 6 occasions over the exposure period (Figure 3.8). DS and SPM were kept suspended by the turbulence generated by oxygen stones. Exposures were run for periods of 8 days, followed by 6 days of depuration. At the sampling times outlined in Figure 3.8, organisms were removed to depuration vessels. Following a 24 h depuration period, isotope activity in the organisms and feces were assessed in order to determine assimilation efficiency and uptake. Water samples were taken at standard intervals to calculate desorption in the aquaria. Figure 3.9 provides a complete sampling summary.

At each sampling, organisms were transferred to depuration containers containing clean water and were allowed to depurate for 24 hrs. After the 24 hr. depuration period, *P. staminea* were sacrificed, the tissue removed from the shell and rinsed in EDTA, blotted and weighed before analysis. *M. balthica* were rinsed with EDTA and weighed before analysis whole; following analysis they were returned to the appropriate treatment. Feces from the 24 hr. depuration period was collected by pipette for analysis.

Figure 3.8 Organism sampling during exposure experiments

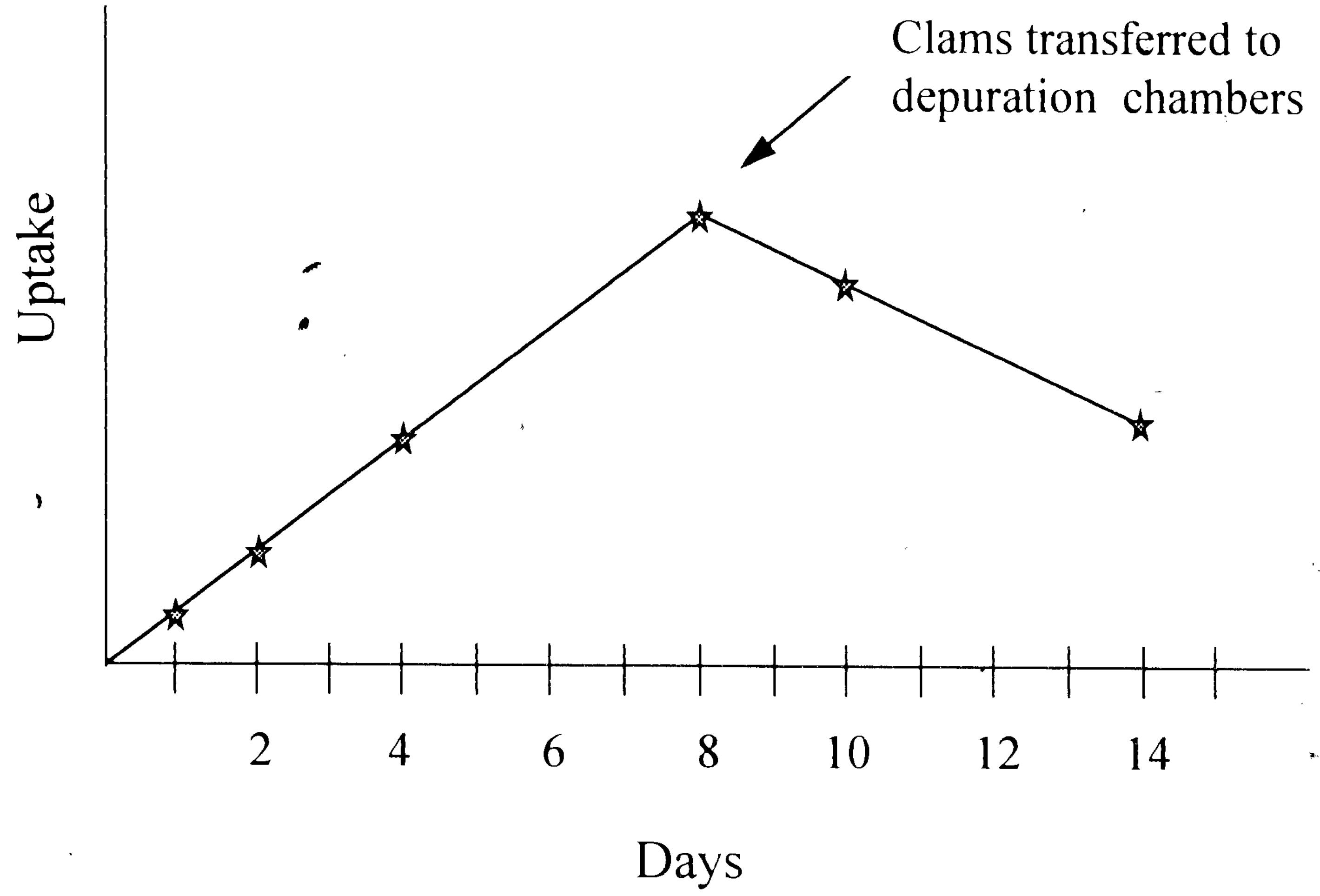
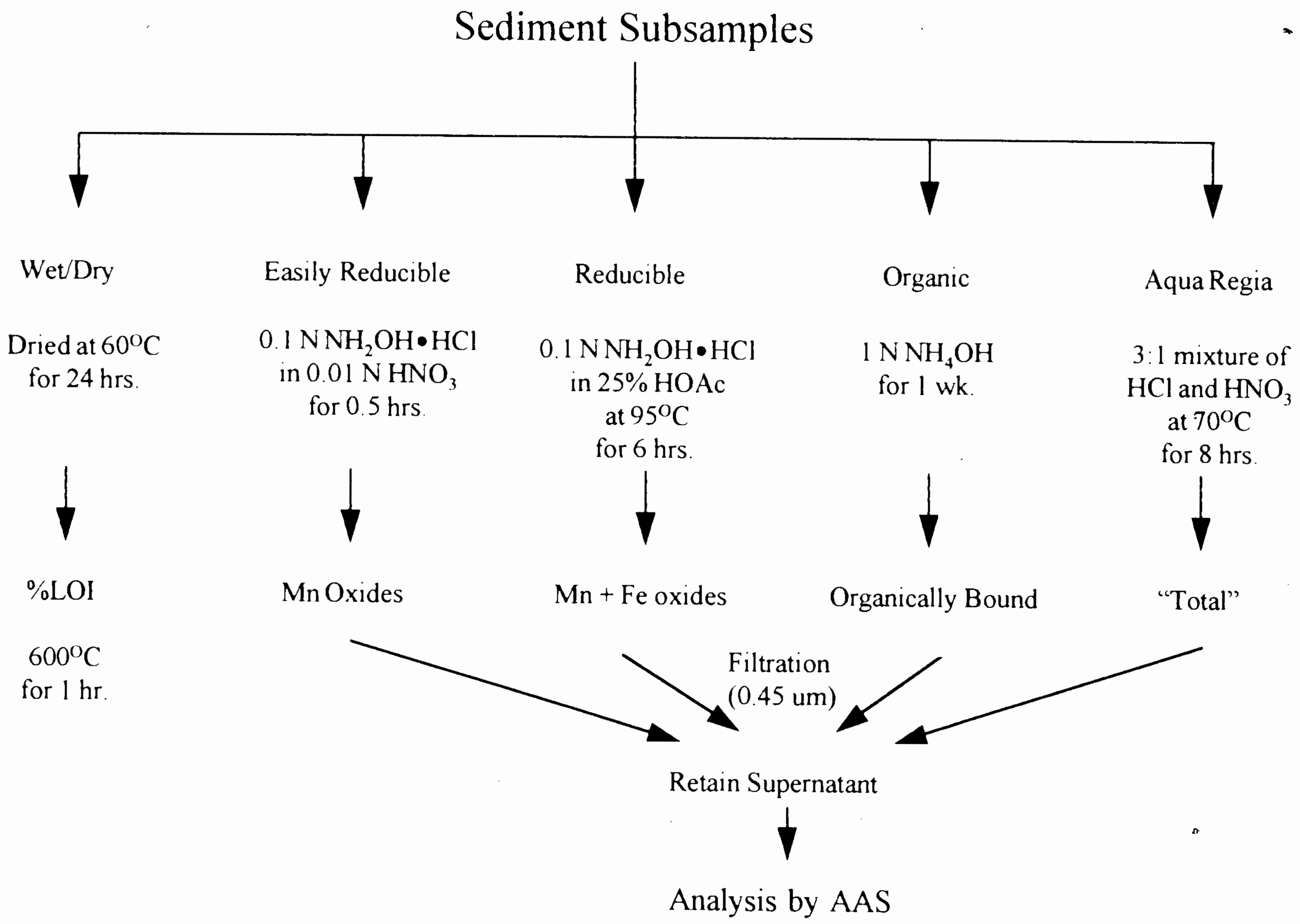


Figure 3.9 Summary of all sampling during exposure experiments



Assimilation experiments were analyzed by the methods of Fisher and Reinfelder (1991) and by simple uptake calculations. Fisher and Reinfelder (1991) used ^{241}Am as an inert tracer and found that it shows essentially no assimilation in marine zooplankton. Thus, they propose that ^{241}Am be used as an inert tracer for the study of gamma emitting isotopes much as ^{51}Cr is used in assimilation studies of beta emitting isotopes (Calow and Fletcher, 1972). Organisms are exposed to the radioisotope of interest and ^{241}Am; the equation used for the determination of assimilation efficiency is:

$$AE = \frac{({}^{109}Cd/{}^{241}Am)food - ({}^{109}Cd/{}^{241}Am)feces}{({}^{109}Cd/{}^{241}Am)food}$$

However, since the experiments run in this study have controls, this equation was modified to:

$$AE = \frac{({}^{109}Cd/{}^{241}Am)food - ([{}^{109}Cd_T - {}^{109}Cd_C]/[{}^{241}Am_T - {}^{241}Am_C])feces}{({}^{109}Cd/{}^{241}Am)food}$$

where T is treatment and C is control. This modified equation was used to account for isotope present in the feces due to uptake of dissolved isotope. The food term of this equation was determined as the amount of isotope added to the slurry minus the amount that desorbs into the water column of the test chamber minus the decay. The feces term was the activity of the control subtracted from the treatment. Measurement of the isotope ratio in the food (sediment) and feces are the only measurements required. Collecting sediment from the aquaria for the equation was impractical due to the manipulations of radioactive samples that this would require. Simple uptake calculations involved the determination of the amount of radioisotope in the organisms at the various time intervals.

4.4 Instrumentation

^{241}Am and ^{109}Cd were detected using an automatic gamma counting system built by the Simon Fraser University Electronics shop. The system uses Nucleus Analyzer Software, and measures gamma radiation with a sodium iodide crystal. Canberra pre-amplifiers and amplifiers supply the signal to the computer. The system is equipped with an automatic sample changer. This system had never been used to measure either isotope before, and had to be set up in order to read both, together, optimally. A 59.6 keV gamma emission of ^{241}Am and an 88 keV gamma emission of ^{109}Cd were read. The system was optimized using standards of each isotope individually and a mixture of the two. Peaks were isolated in comparison with the known ^{125}I 35 keV peak. Optimal detection is a compromise between efficiency and discrimination of the two peaks. The optimal setting was determined to be 820V on the power supply, and an amplifier setting of 3 K. The peaks were read in the "quarters" mode for better resolution, with a gain of 1024 channels and no offset. Under the conditions noted above, the ^{241}Am peak was found in channels 65 to 111, and the ^{109}Cd peak in channels 125-210. The peaks were also calibrated for the energy of ^{109}Cd and ^{241}Am. Efficiency for ^{109}Cd was determined to be 4.33%, while the efficiency of ^{241}Am was 51.99%.

4.5 Supportive Experiments

In both sets of experiments, effort was made to determine radiotracer partitioning among sediments, water, organisms, and the exposure vessels. Water samples were taken throughout the experiments; at the beginning, filtered and whole water samples were analyzed on intervals summarized in Figure 3.8. Following completion of the experiments, water was diluted and disposed of, sediments were collected for analysis, and swipe tests of the aquaria were used in determining the mass balance of radiotracer.

4.6 Statistical Analyses

Statistical analyses were carried out using SAS, version 6.08. Comparison of assimilation was done using t-tests; uptake was analyzed using ANOVA (SAS, 1990) with Tukey and Bonferroni multiple contrasts (P=0.05 experimentwise). Isotope distribution and isotope desorption were analyzed using Bonferroni t-tests.

5.0 REFERENCES

American Public Health Association (APHA). 1992. Standard Methods for the examination of water and wastewater. Prepared and published by the American Public Health Association, American Water Works Association, and Water Pollution Control Federation. American Public Health Association, Washington, DC. 874 pp.

Bendell-Young, L.I., M. Dutton and F.R. Pick. 1992. Contrasting two methods for determining trace metal partitioning in oxidized lake sediments. Biogeochemistry 17: 205-219.

Calow, P. and C.R. Fletcher. 1972. A new radiotracer technique involving ^{14}C and ^{51}Cr, for estimating the assimilation efficiencies of aquatic, primary producers. Oecologia 9: 155-170.

Chao, T.T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am. Proc. 36: 764-768.

Etcheber, H. and J.M. Jouanneau. 1980. Comparison of the different methods for the recovery of suspended matter from estuarine waters: deposition, filtration and centrifugation; consequences for the determination of some heavy metals. Estuar. Coast. Mar. Sci. 11: 701-.

Fisher, N.S. and J.R. Reinfelder. 1991. Assimilation of selenium in the marine copepod *Acartia tonsa* studied with a radiotracer method. Mar. Ecol. Prog. Ser. 70: 157-164.

Fraser, C.M. and G.M. Smith. 1928. Notes on the ecology of the little neck clam, *Paphia staminea* Conrad. Trans. Royal Soc. Can.

Harvey, R.W. and S.N. Luoma. 1985. Separation of solute and particulate vectors of heavy metal uptake in controlled suspension-feeding experiments with *Macoma balthica*. Hydrobiologia 121: 97-102.

Horowitz, A.J., F.A. Rinella, P. Lamothe, T.L. Miller, T.K. Edwards, R.L. Roche and D.A. Rickert. 1990. Variations in suspended sediment and associated trace element concentrations in selected riverine cross-sections. Environ. Sci. Technol. 24: 1313-1320.

Horowitz, A.J.. 1986. Comparison of methods for the concentration of suspended sediment in river water for subsequent chemical analysis. Environ. Sci. Technol. 20: 155-160.

Horowitz, A.J., K.A. Elrick and R.C. Hooper. 1988. A comparison of instrumental dewatering methods for the separation and concentration of suspended sediment for subsequent trace metal analysis. Hydrol. Process. 2: 163-184.

Knighton, D.. 1984. Fluvial forms and processes. Edward Arnold Publishers. 218pp.

Luoma, S.N. 1986. A comparison of two methods for determining copper partitioning in oxidized sediments. Mar. Chem. 20: 45-59.

Ongley, E.D. and D.P Blachford. 1982. Applications of continuous-flow centrifugation to contaminant analysis of suspended sediment in fluvial systems. Environ. Technol. Lett. 3: 219-228.

Ongley, E.D., B.G. Krishnappan, I.G. Droppo, S.S. Rao and R.J. Maguire. 1992. Cohesive sediment transport: emerging issues for toxic chemical management. Hydrobiologia 235/236: 177-187.

Ongley, E.D., M.C. Bynoe and J.B. Percival. 1982. Physical and geochemical characteristics of suspended solids, Wilton Creek, Ontario. Hydrobiologica 91: 41-57.

Rees, T.F., J.A. Leenheer, and J.F. Ranville. 1991. Use of a single-bowl continuous-flow centrifuge for dewatering suspended sediments: effects on the sediment physical and chemical characteristics. Hydrol. Process. 5: 201-214.

Santiago, S., R.L. Thomas, L.J. Loizeau, G. Larbaigt, C. Corvi, D. Rossel, J. Tarradellas, L.H. McCarthy and J.P. Vernet. 1992. Particle size characteristics of suspended and bed sediments in the Rhone River. Hydrological Processes 6: 227-240.

Santiago, S., R.L. Thomas, J.L. Loizeau, P.Y. Favarger and J.P. Vernet. 1990. Further discussion on the intercomparison of the trace metal concentrations and particle size of fluvial sediment recovered from two centrifuge systems. Hydrological Processes 6: 227-240.

SAS, 1990. SAS/STAT user's guide, Version 6, Fourth Edition. SAS Institute, Cary, North Carolina.

Schoer, J.H.. 1990. Determination of the origin of suspended matter and sediments in the Elbe Estuary using natural tracers. Estuaries 13: 161-172.

Sinclair, P.L., R. Beckett and B.T. Hart. 1989. Trace elements in suspended particulate matter from the Yarra River, Australia. Hydrobiologia 176/177: 239-251.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7): 844-851.

Warren, L.A.. 1994. Trace metal complexation by suspended particulates in an urban river. Ph.D. Thesis, Department of Zoology, University of Toronto. 165 pp.

CHAPTER 4: PHYSICO-CHEMICAL CHARACTERISTICS AND METAL GEOCHEMISTRY OF THE FRASER RIVER ESTUARY

This chapter presents and contrasts the geochemical characteristics, metal concentration, and metal distribution of SPM and DS. It also summarizes the characteristics of the physico-chemical environment from which the sediments were collected and the variability of both physico-chemical conditions and sediment geochemistry over the course of the study.

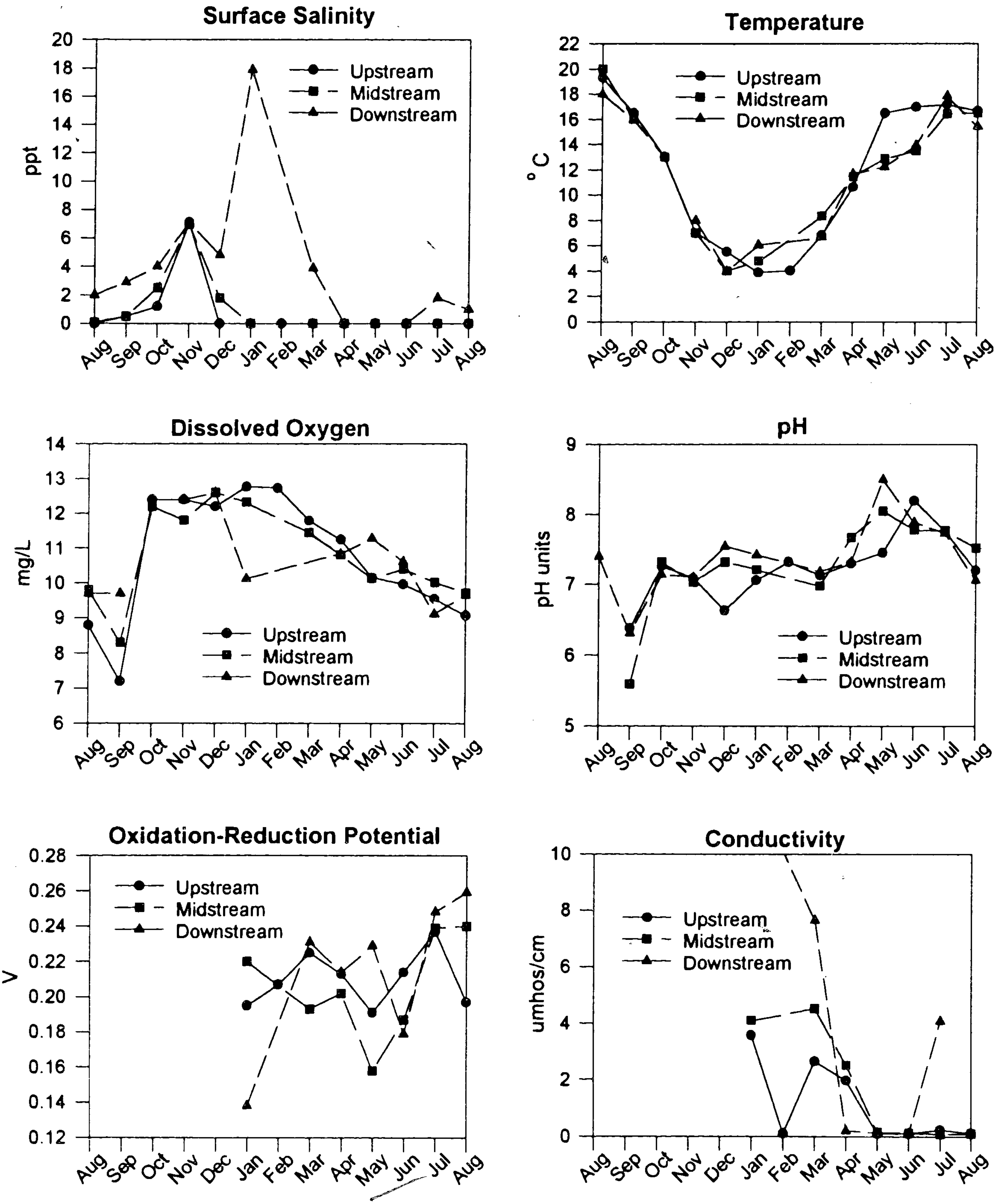
1.0 RESULTS

The following results were obtained on 36 sampling excursions over 12 months (August 1994 to August 1995). Water quality parameters were measured at each sampling. A total of 216 sediments were collected, each analyzed for 6 different metals in 4 extracts.

1.1 Physico-chemical Variables

The physico-chemical variables of salinity, temperature, dissolved oxygen and pH were measured on all sampling occasions over the period of August 1994 to August 1995 at each site (Figure 4.1). From January to August 1995, conductivity and oxidation/reduction potential were also measured (Figure 4.1). Fraser River discharge showed normal seasonal variation, with storm event peaks over shorter time scales (Figure 4.2). Expected seasonal trends of temperature and salinity were noted. Salinity maxima and temperature minima occurred in the winter (low flow). Dissolved oxygen maxima occurred in the winter. An inverse relationship with temperature (r=-0.81, P=0.0001, N=36) was observed. Maxima in pH were observed in the months of May and June concurrent with the spring freshet. A positive relationship between pH and discharge was observed (r=0.55, P=0.0004, N=37). Oxidation-reduction potential was always positive, indicative of an oxidizing environment. Turbidity measurements (Figure 4.3) show maxima in the months of May and June, with a positive relationship with discharge (r=0.78, P=0.0001, N=27). The study areas were generally within the

Figure 4.1 Physico-chemical characteristics of the Fraser River Estuary, 1994-1995



Surface Salinity

Temperature

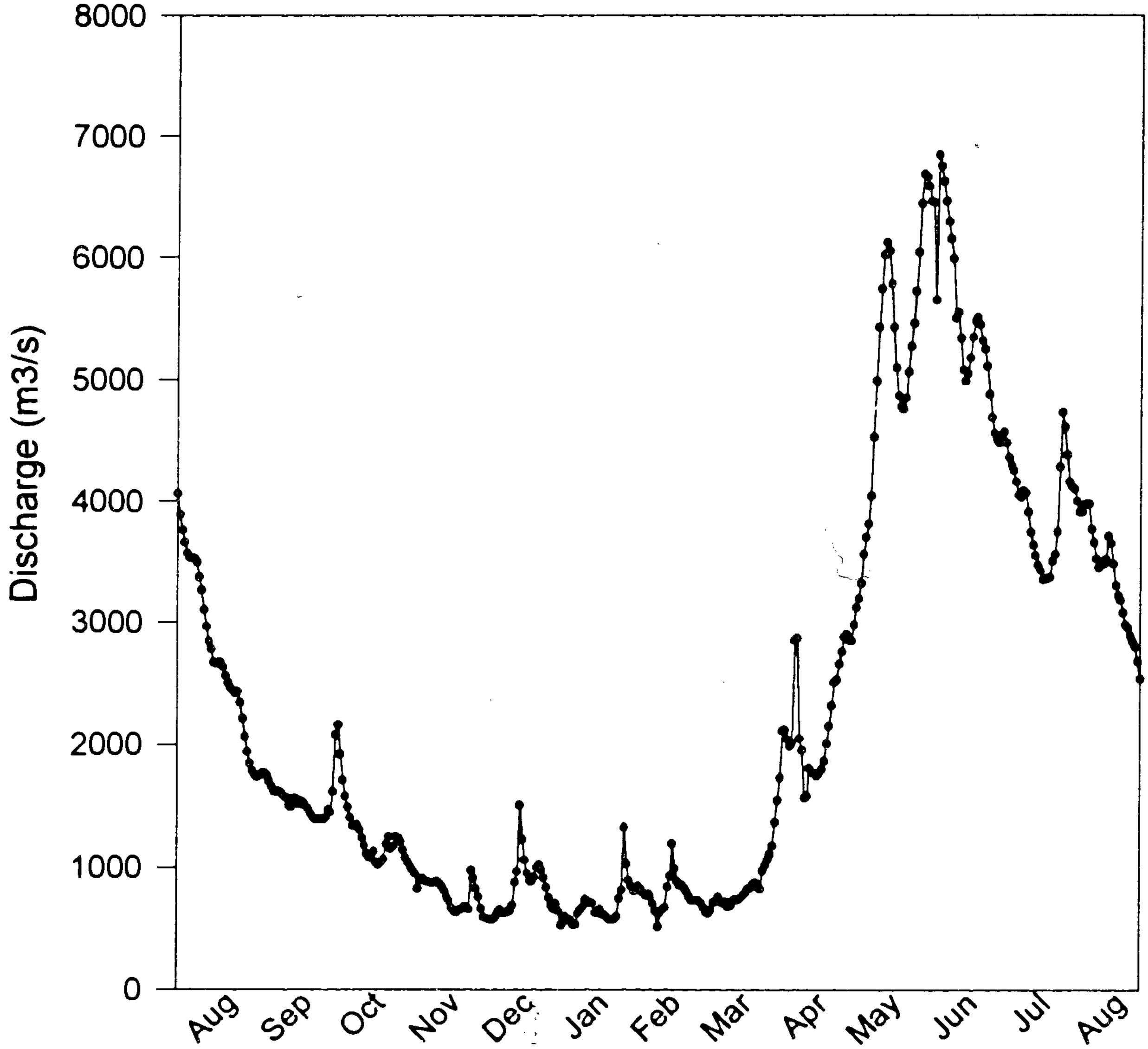
Dissolved Oxygen

pH

Oxidation-Reduction Potential

Conductivity

Figure 4.2 Fraser River discharge, 1994-1995, measured at Hope by the Water Survey of Canada



turbidity maximum of the estuary as determined by turbidity measurements taken during three estuarine cruises. For all measured parameters except salinity and conductivity, there was little difference between the three sites (Figures 4.1 and 4.3).

1.2 SPM Concentration

The total amount of SPM recovered from rotor following a centrifugation run was used as a measure of SPM concentration in the river (Figure 4.4). SPM concentrations were below 10 mg/L (wet weight) from November 1994 to March 1995. Concentrations subsequently rose with discharge to 20 to 70 mg/L from June to August; consistent with turbidity observations. The trends of particulate concentrations among the three sites were similar; no site had consistently greater SPM concentrations than others. SPM concentrations were controlled by discharge (Figure 4.5), with significant positive r values (Table I). A hysteresis was observed between SPM concentration and discharge (Figure 4.6); the pattern for each site being somewhat different. No significant relationships between tide and SPM concentration were found.

Table I: Correlation between discharge and SPM concentration (mg/L)

Correlation	*N*	*r*	*P*
Discharge vs. SPM (Upstream)	12	0.74	.0055
Discharge vs. SPM (Midstream)	12	0.84	.0006
Discharge vs. SPM (Downstream)	12	0.80	.0020
Discharge vs. SPM (Pooled)	36	0.77	.0001

1.3 Sediment matrix features of SPM and DS

Features of the sediment matrix were determined over the course of the sampling. These included particle size, organic content as determined by loss on ignition, and the oxides of iron and manganese (operationally defined as reducible iron [rFe] and easily reducible manganese [erMn], respectively).

Figure 4.3 Turbidity measurement in the Fraser River Estuary, 1994-1995

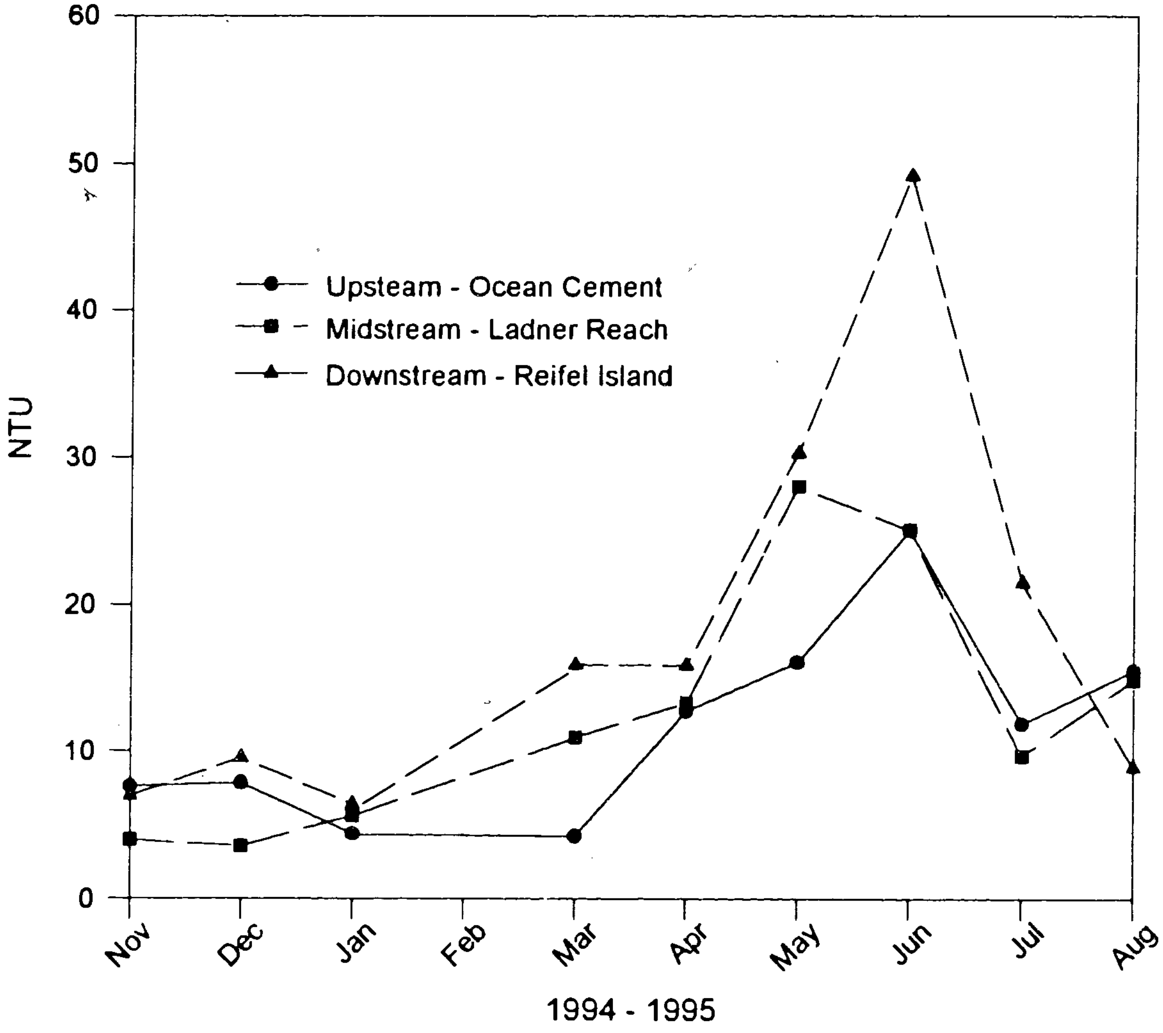


Figure 4.4 Fraser River Estuary particulate concentration, 1994-1995

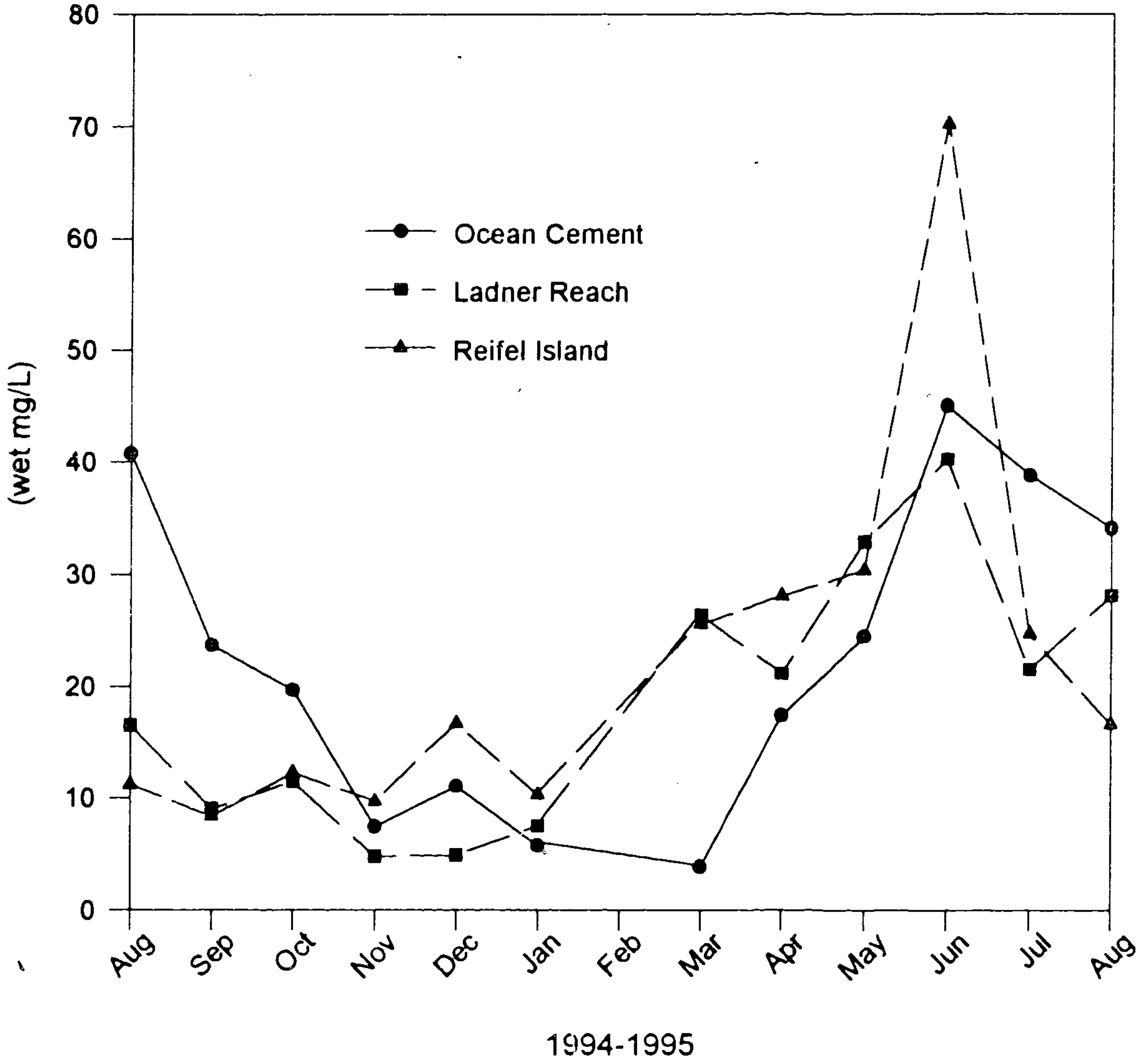


Figure 4.5 Relationship between discharge and SPM in the Fraser River Estuary, 1994-1995

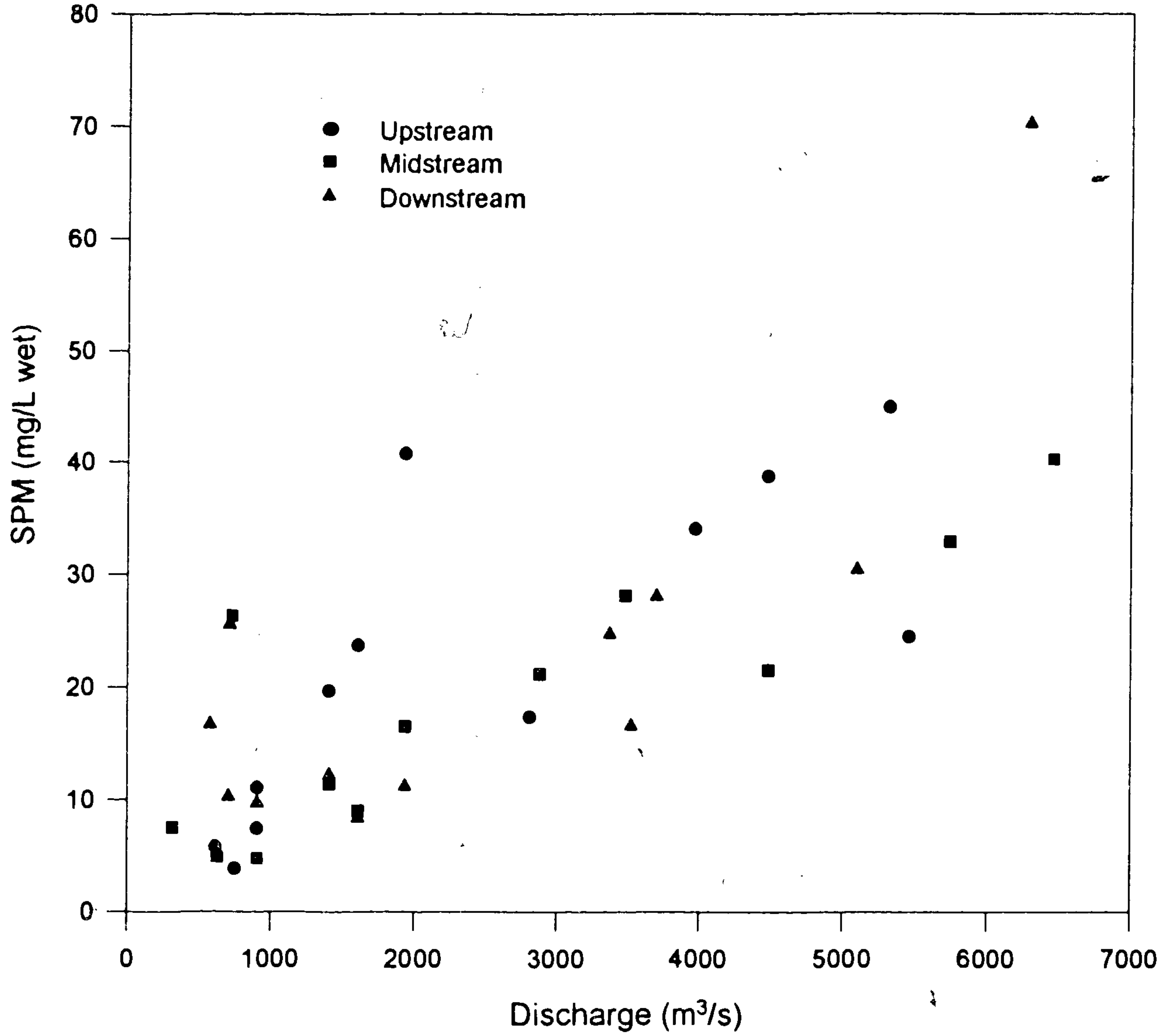
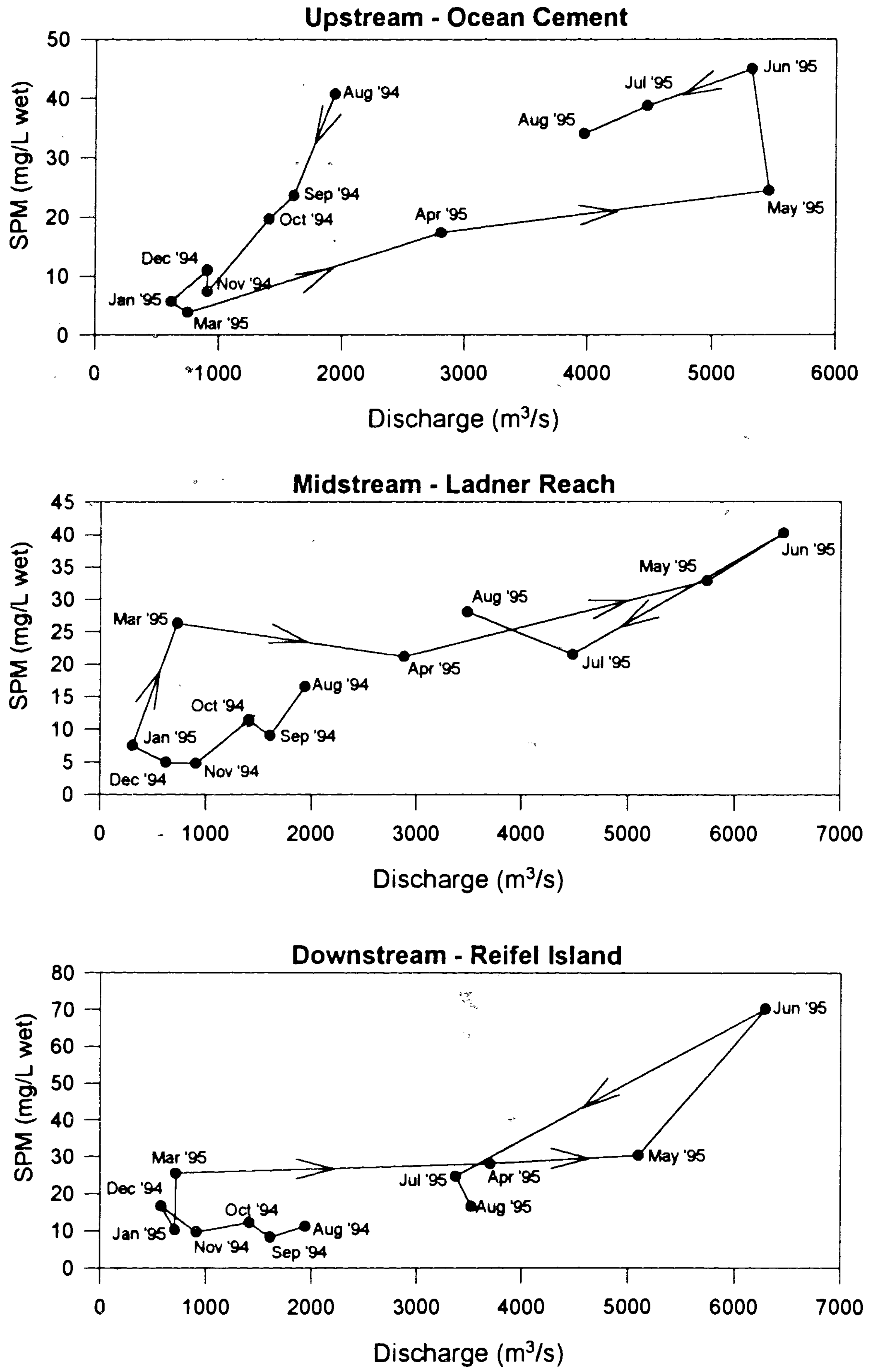


Figure 4.6 Seasonal hysteresis in the discharge-SPM relationship, 1994-1995



1.3.1 Particle Size

Particle sizes for SPM were obtained in the months of May, June, and August, with the addition of March at one site (Figure 4.7). In other months, the yield of SPM was not sufficient to allow particle size analysis. The particle size of SPM was uniform over time and among the upstream and midstream sites. These sites had mean particle sizes as summarized in Table II, with a skew to the right. The downstream site showed a bimodal distribution in all but one month (August), with one node at approximately 5 µm and the second at 20-25 µm.

Table II: Weighted mean particle size of Fraser River Estuary SPM

Month	*Site*	*Weighted Average (µm)*
May	1	11.90
	2	12.51
	3	8.96
June	1	11.50
	2	12.27
	3	11.04
Aug	1	11.85
	2	10.72
	3	10.55

Deposited sediment was characterized as the percent clay (<2.0 µm), silt (between 2.0 and 62.5 µm), and sand (>62.5 µm); percent silt was always the dominant fraction (Figure 4.8). No statistically significant differences between the percentages of either clay or sand were found between the three sites. However, ANOVA and Tukey test results of the percent silt (proportions arcsine transformed) indicate that the sites are different (N=33, F=6.30, P=0.005) and that the mid-estuary site has a significantly higher proportion of silt in DS than do the two other sites (at the P=0.05 level).

Figure 4.7 Particle size of Fraser River Estuary suspended particulate matter, 1994-1995

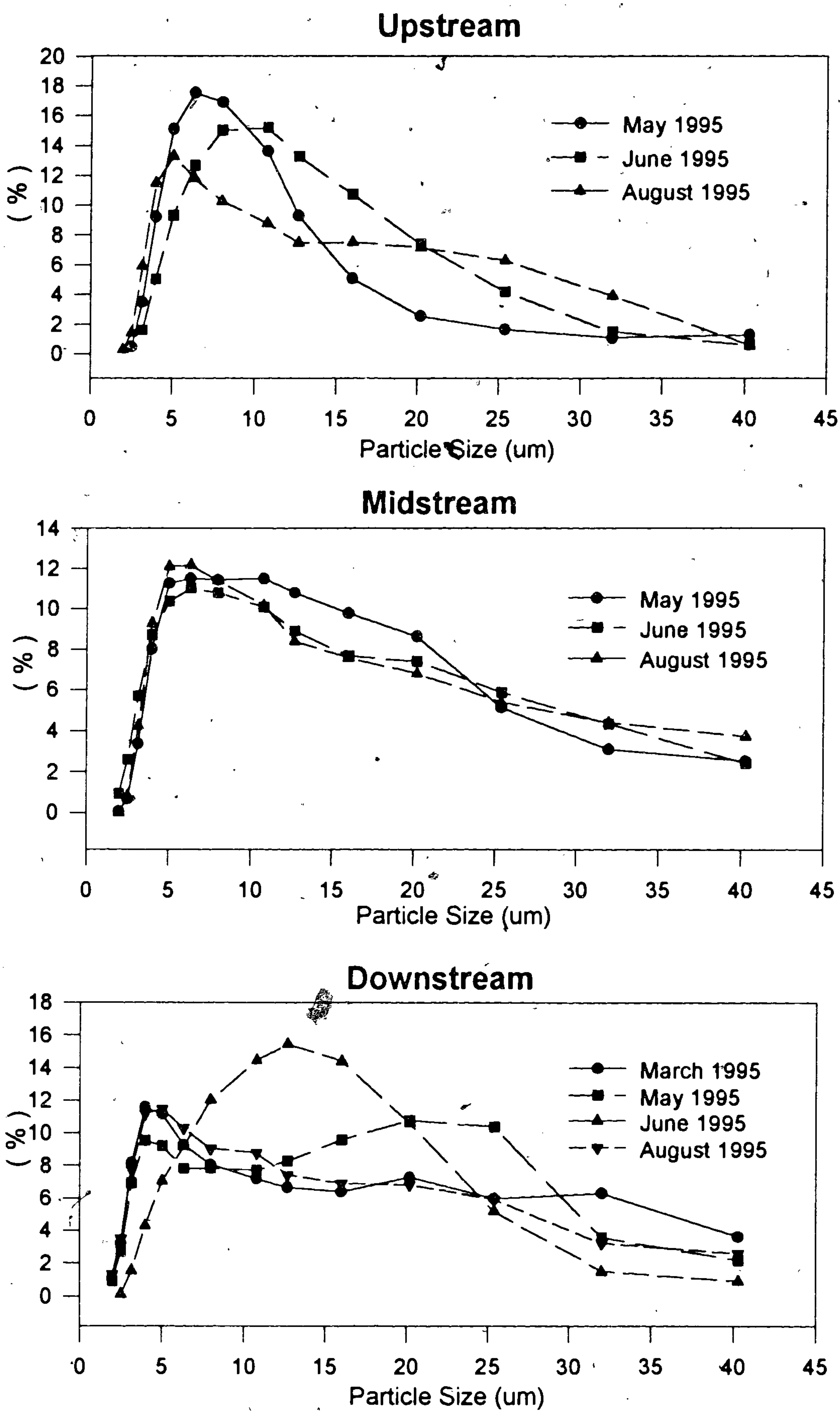
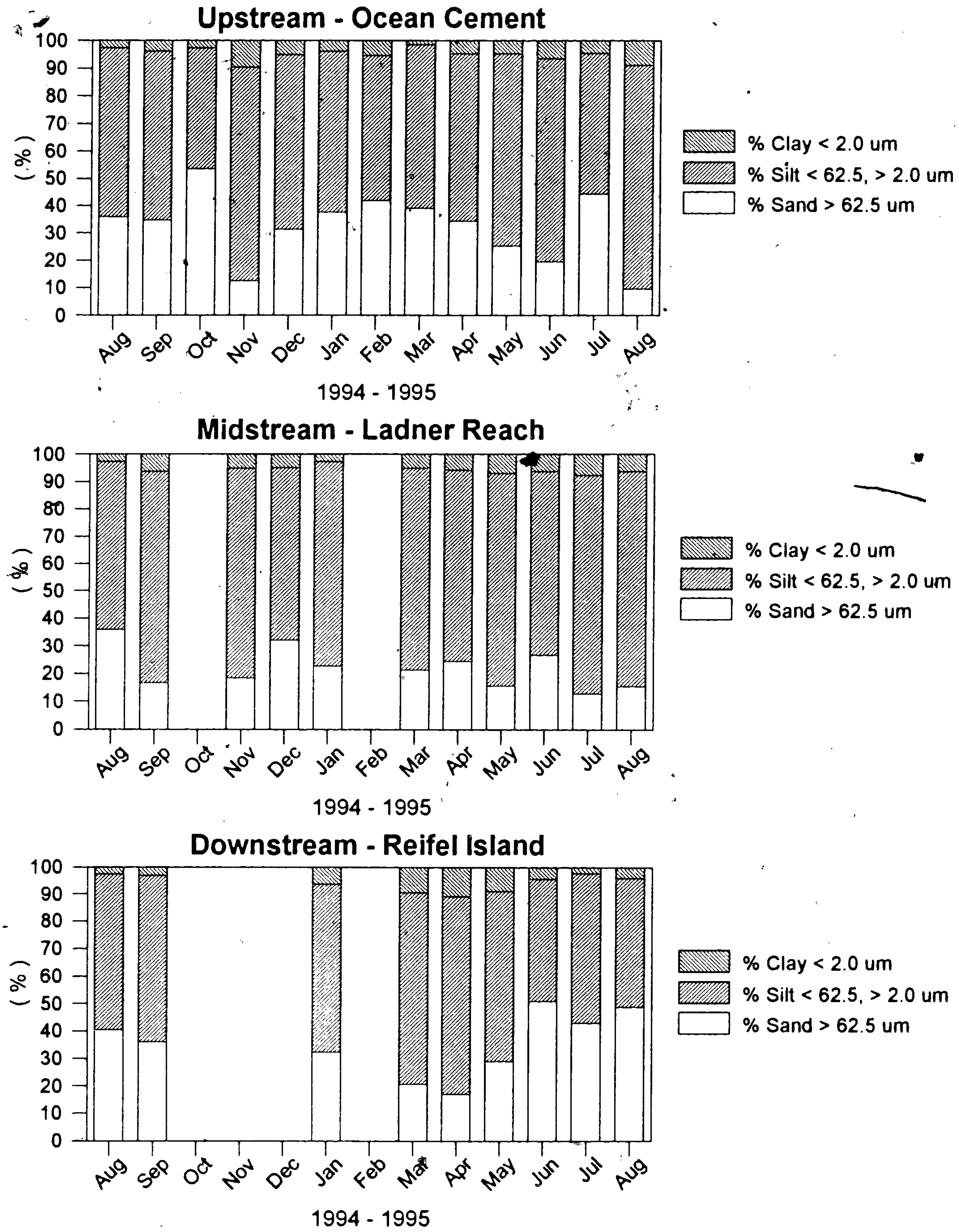


Figure 4.8 Particle size of Fraser River Estuary deposited sediments, 1994-1995



1.3.2 Organic Content

Organic content and the concentrations of metal oxides in the sediments of the Fraser River Estuary are summarized (sites grouped) in Table III and Figure 4.9.

Table III: Matrix features of SPM and DS of the Fraser River Estuary

	LOI		*rFe*		*erMn*	
	SPM (%)	*DS* (%)	*SPM* (mg/kg)	*DS* (mg/kg)	*SPM* (mg/kg)	*DS* (mg/kg)
Aug 94	3.14 ± 0.30	5.94 ± 1.35	7710 ± 1240	4510 ± 898		31.6 ± 11.7
Sep 94	3.55 ± 0.24	4.61 ± 0.71	8580 ± 261	4640 ± 698	157 ± 19.0	80.0 ± 15.5
Oct 94	4.61 ± 0.77	5.10 ± 2.04	11000 ± 4770	4120 ± 509	244 ± 71.0	56.3 ± 7.6
Nov 94	8.46 ± 2.90	4.43 ± 0.39	42000 ± 14800	6760 ± 554	346 ± 124	119 ± 25.4
Dec 94	16.27 ± 2.51	5.23 ± 0.63	29100 ± 7330	7030 ± 605	147 ± 23.3	75.3 ± 9.2
Jan 95	23.09 ± 5.93	4.65 ± 1.52	53100 ± 9470	7550 ± 227	384 ± 53.7	96.1 ± 12.6
Mar 95	13.15 ± 1.80	3.48 ± 0.56	38000 ± 9950	8120 ± 547	184 ± 102	66.6 ± 16.5
Apr 95	8.30 ± 0.69	4.33 ± 0.42	11100 ± 2320	6310 ± 222	129 ± 16.7	106 ± 6.6
May 95	9.30 ± 1.87	4.46 ± 0.29	7810 ± 485	5940 ± 312	354 ± 31.8	117 ± 25.0
Jun 95	5.81 ± 0.44	4.63 ± 0.44	7570 ± 424	6270 ± 443	123 ± 21.5	91.3 ± 12.7
Jul 95	4.20 ± 0.21	3.38 ± 0.13	7390 ± 1054	4710 ± 407	301 ± 44.4	125 ± 11.0
Aug 95	6.62 ± 1.58	4.41 ± 0.35	9280 ± 783	5660 ± 301	293 ± 103	184 ± 20.6

From the trends noted in Figure 4.9, it is evident that SPM and DS differ and that there is a seasonal influence. Data in all the following analyses were arcsine transformed. ANOVA of arcsine transformed LOI revealed no statistically significant intersite differences for either deposited (N=109, F=1.51, P=0.22) or suspended sediment (N=75, F=1.76, P=0.18). Two-way ANOVA on the pooled data indicate significance of month, sediment type, and the interaction (Table IV).

Figure 4.9 Concentrations of matrix features of Fraser River Estuary sediments, 1994-1995 (stars indicate statistical significance in SPM vs. DS comparison; sites grouped)

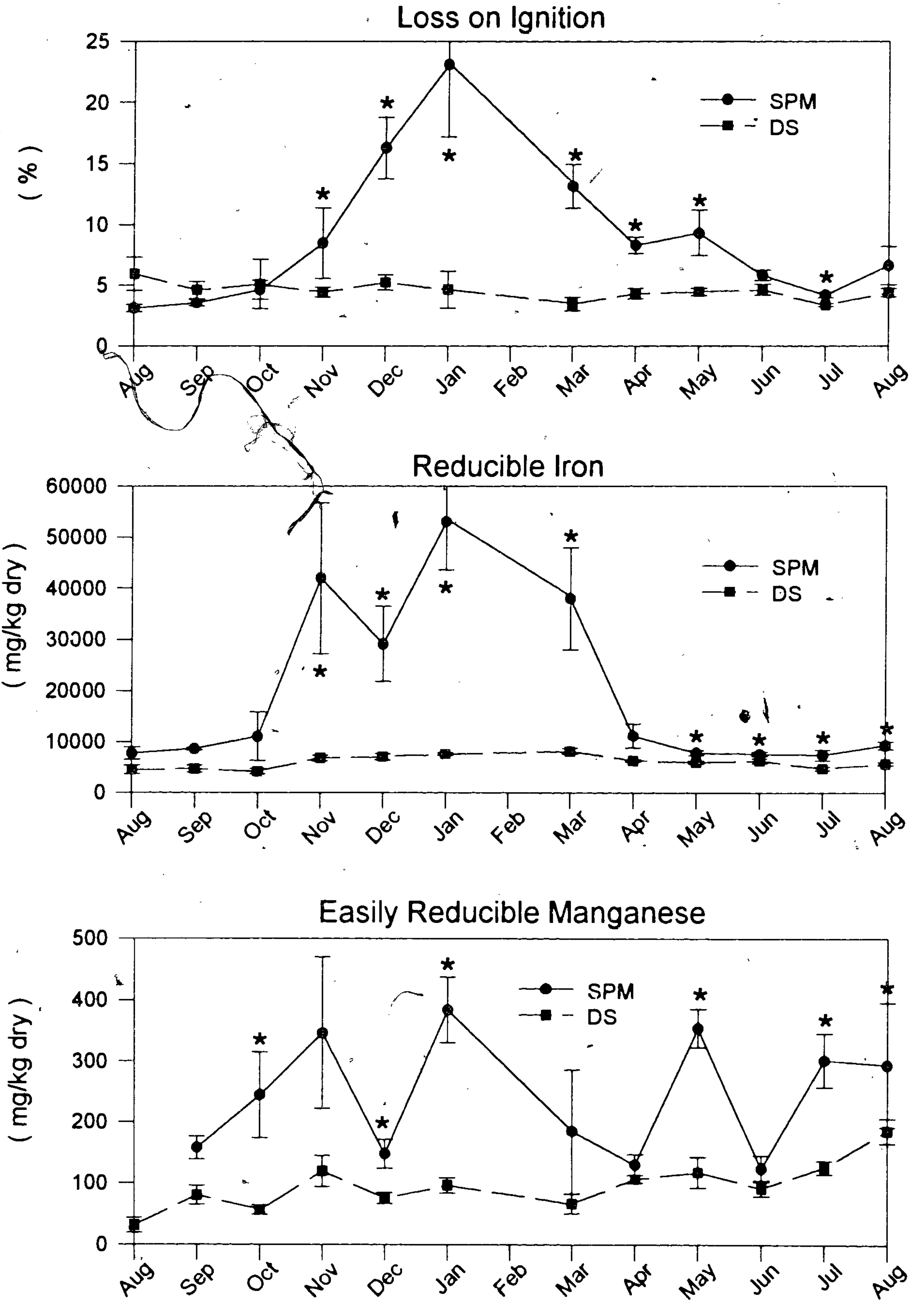


Table IV: Two-way ANOVA for Organic Content

N = 184	*df*	*F*	*P*
Month	12	6.84	0.0001
Type	1	81.94	0.0001
*Month*Type*	12	8.68	0.0001

ANOVA with multiple contrasts (Tukey) was subsequently employed to determine if differences in organic content occurred among different month, and if so, which months. These contrasts were performed for each sediment type. For DS, no significant differences occurred with month of sampling (N=109, F=1.23, P=0.27). For SPM, this difference was significant (N=75, F=8.45, P=0.0001). Tukey testing (P=0.05) revealed the following differences in organic content (from high to low):

```
              ---------------------------------
      -----------
SPM:  jan dec mar may nov apr aug95 jun oct jul sep aug94
          ------------------------------
                  ---------------------------------------
```

The organic content of DS is consistent over the course of the year, but for SPM shows a distinct seasonal trend. SPM organic content is lowest during high flow conditions (May through July) and highest under the lowest flow conditions (November to January). Correlations between discharge and SPM organic content and the SPM concentrations and SPM organic content are summarized in Table V. There is a weak inverse relation with discharge and SPM concentration, which are not significant (P = 0.118 and P = 0.082, respectively). A significant negative relationship between organic content in suspended sediment and temperature was observed (r=-0.77, P=0.0001, N=35). No significant relationships between any of the physical variables and the organic content of DS were discernable.

Table V: Correlations of mean SPM matrix features with discharge and SPM concentration

Correlation	*N*	*r*	*P*
Discharge vs. SPM LOI	37	-0.26	0.118
Discharge vs. SPM rFe	39	-0.53	0.001
Discharge vs. SPM erMn	36	0.16	0.351
SPM Concentration vs. SPM LOI	37	-0.29	0.082
SPM Concentration vs. SPM rFe	39	-0.53	0.001
SPM Concentration vs. SPM erMn	36	-0.06	0.722

1.3.3 Metal Oxide Content

The concentrations of reducible iron (rFe; an operationally defined analogue of iron oxide) and easily reducible manganese (erMn; an operationally defined analogue of manganese oxide) are summarized in Table III and Figure 4.9. Reducible iron shows the same trends as observed for organic matter. This seasonal trend is not evident for easily reducible manganese.

ANOVA of log transformed rFe concentration at the three different sites reveals no statistically significant differences for either deposited (N=110, F=1.98, P=0.14) or suspended sediment (N=87, F=2.47, P= 0.09). Two-way ANOVA on the pooled data indicate significance of month, sediment type, and the interaction term (Table VI).

Table VI: Two-way ANOVA for rFe Content

N = 197	*df*	*F*	*P*
Month	12	21.62	0.0001
Type	1	188.85	0.0001
*Month*Type*	12	8.20	0.0001

ANOVA with multiple contrasts (Tukey) on each sediment type indicated that significant differences occurred among month for both DS (N=110, F=6.10, P= 0.0001) and SPM (N=84, F=14.47, P=0.0001). For DS and SPM, Tukey's a-posteriori test revealed the following differences in rFe concentration (from high to low):

```
                 -----------------------------
     ---------------------------------
DS:  mar jan dec nov apr jun may aug95 jul sep oct aug94
             -----------------------------
                     -----------------------------------
```

```
     --------------- -----------------------------------
SPM: jan nov mar dec apr oct aug95 may aug94 jun jul sep
                 ---------------------
```

The rFe concentration of SPM is generally greater than that of DS, especially during low flow conditions (Figure 4.9). It is noteworthy that for rFe, a seasonal trend in DS is also noted (Figure 4.10) where it is noted only for SPM with organic content. Reducible iron in SPM shows significant inverse relationships with discharge (r=-0.53, P=0.001, N=39), temperature (r=-0.81, P=0.0001, N=36), and SPM concentration (r=-0.53, P=0.001, N=39). In DS, reducible iron showed a significant inverse relation with temperature (r=-0.60, P=0.0001, N=35).

ANOVA of log transformed erMn content at the three different sites reveals no statistically significant differences for either deposited (N=110, F=1.73, P=0.18) or suspended sediment (N=84, F=1.65, P= 0.20). Two-way ANOVA on the pooled data indicate significance of month, sediment type, and the interaction term (Table VII).

Figure 4.10 Concentrations of the matrix features in DS only, 1994-1995

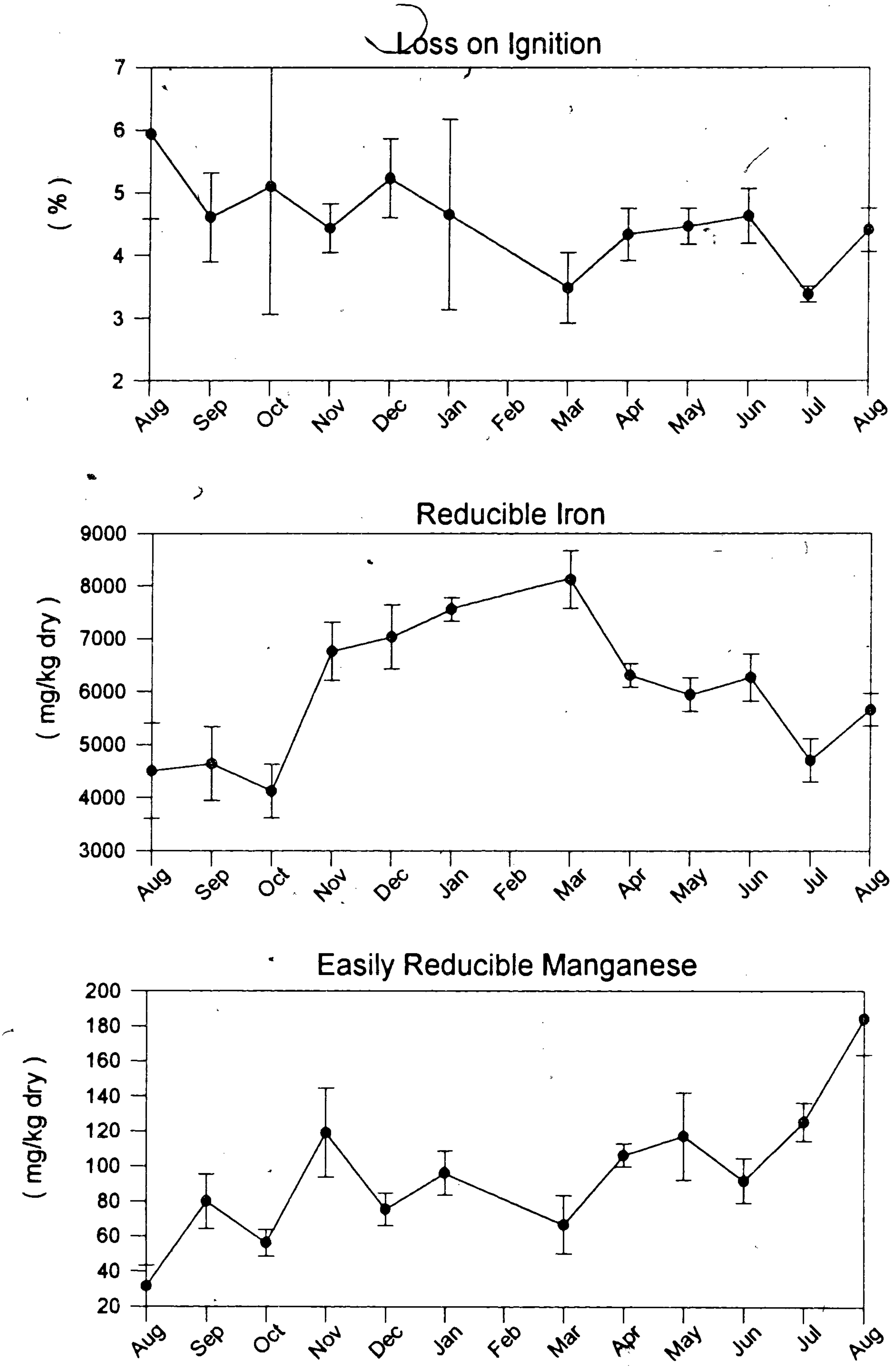


Table VII: Two-way ANOVA for erMn Content

N = 194	*df*	*F*	*P*
Month	12	6.84	0.0001
Type	1	81.94	0.0001
*Month*Type*	12	8.68	0.0001

ANOVA with multiple contrasts (Tukey) on each sediment type indicated firstly that significant differences occurred among month for both DS (N=110, F=21.12, P=0.0001) and SPM (N=84, F=10.12, P=0.0001). For DS and SPM, Tukey's a-posteriori test revealed the following differences in erMn concentration (from high to low):

```
      -------------------------------- ------------------
 DS:  aug95 jul apr may nov jan jun dec oct mar aug94 sep
             ----------------------------------
```

```
          -----------------------------------      ----
   SPM:  jan may nov aug95 jul oct dec jun apr mar sep
                   --------------------------------
```

For erMn, no seasonal trend in SPM and DS differences are evident as in organic content and rFe concentration (Figure 4.9). In both SPM and DS, erMn is not significantly correlated with temperature, discharge or SPM concentration.

1.3.4 Relationships between matrix features

The relationships between the matrix features are summarized in Table VIII. In SPM, LOI and rFe, and rFe and erMn are significantly correlated. In DS, the percentage clay content is positively correlated with all three matrix features (LOI, rFe and erMn). In addition, rFe an erMn are positively correlated in DS.

Table VIII: Correlations between mean matrix features

A: SPM

Correlation	*N*	*r*	*P*
LOI vs. rFe	37	0.65	0.0001
LOI vs. erMn	34	0.27	0.1212
rFe vs. erMn	36	0.38	0.0239

B: DS

Correlation	*N*	*r*	*P*
Clay vs. LOI	35	0.32	0.0624
Clay vs. rFe	35	0.50	0.0024
Clay vs. erMn	35	0.24	0.1669
LOI vs. rFe	37	0.21	0.2207
LOI vs. erMn	37	-0.15	0.3718
rFe vs. erMn	37	0.24	0.1517

1.4 Metal Concentrations

Metal concentrations over the sampling period in the different extracts employed are summarized in Table IX, Figures 4.11 through 4.16 and Appendix 3 (by month). For the purposes of these comparisons, metal concentrations at the three sites were pooled. Two-way ANOVA was employed to determine the significance of month, sediment type, and interaction for each phase of each metal (summarized in Table X). In addition, multiple contrasts were performed to determine the statistical significance of the SPM versus DS comparison (Bonferroni t-tests, P=0.05 experimentwise, Table XI). All metals were generally found to be present in higher concentrations in SPM than in DS on a concentration per dry weight basis, although the frequency and magnitude of this difference varied with metal and phase. In addition, the metal concentrations in SPM exhibit the strong seasonal influence evident for the sediment matrix features (section 1.3). Differences between the two sediments are most extreme in the winter months, coincident with the highest SPM organic and iron oxide (rFe) content.

1,4.1 Cadmium

Cadmium was analyzed by graphite furnace AAS in the months of December, March, May, June, and August (Table IX, Figure 4.11, Appendix 3). Only the easily reducible and reducible phases were analyzed; concentrations in the organic extract were always below the limit of detection (Appendix 2). Concentrations in the easily reducible phase are higher in SPM than in DS (Table IX, Figure 4.11, Appendix 3). Of the months for which cadmium was analyzed, the highest concentration in the easily reducible fraction was 6.18 ± 1.61 mg/kg in SPM in December while the highest concentration in the reducible fraction was 0.845 ± 0.242 mg/kg in SPM in August (Appendix 3). Cadmium concentrations in the reducible extract of SPM were not much higher than in the easily reducible extract, with a negative reducible value in SPM occurring in March. In DS, the concentrations in the reducible phase were always greater than zero. Figure 4.11 highlights the near order of magnitude difference in the concentration of easily reducible cadmium in the SPM versus the DS. Two-way analysis of variance indicated a significant difference in easily reducible Cd concentration in the two sediment types (Table X). There was no significant difference in reducible cadmium between

Table IX: Metal concentrations in Fraser River Estuary SPM and DS, 1994-1995 (sites pooled)

Metal	Phase	Deposited Sediment					Suspended Particulate Matter				
		N	Mean (mg/kg)	SE (mg/kg)	Q 1* (mg/kg)	Q 3* (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	Q 1* (mg/kg)	Q 3* (mg/kg)
Cadmium	Easily Reducible	42	0.359	0.019	0.265	0.447	42	3.92	0.714	1.94	4.27
	Reducible	44	0.203	0.045	0.007	0.304	44	0.017	0.479	-0.341	0.929
Copper	Easily Reducible	111	4.87	0.39	1.55	7.66	84	44.1	10.1	4.12	41.3
	Reducible	111	3.26	0.43	-0.19	6.72	87	12.4	3.07	7.37	22.1
	Organic	106	4.50	0.29	2.44	6.06	83	43.1	7.70	12.4	47.0
	Residual	105	17.8	0.87	13.4	20.5	81	-1.60	9.78	-3.14	27.1
Iron	Easily Reducible	111	951	104	469	1210	84	2520	409	454	3070
	Reducible	110	5020	208	3620	6250	87	17000	2050	6360	20400
	Organic	111	48.2	4.7	15.5	57	82	642	111	39	750
	Residual	105	18800	600	16100	22400	83	25500	1560	19100	31300
Lead	Easily Reducible	67	2.4	0.2	0.8	3.6	48	23.2	3.5	1.6	36.3
	Reducible	75	1.5	0.2	0.5	3.1	51	8.1	1.9	1.3	15.5
	Residual	105	3.9	1.8	0.8	3.1	81	18.3	9.8	2.5	9.1
Manganese	Easily Reducible	110	90.9	5.9	46	120	84	233	18	109	307
	Reducible	111	171	9	105	232	87	379	22	236	483
	Organic	104	21.7	2.1	7.4	27.0	82	144	19	32	172
	Residual	107	377	28	231	515	83	668	85	155	986
Zinc	Easily Reducible	84	8.42	1.42	3.70	8.55	78	172	30.0	55.6	178
	Reducible	84	13.0	1.25	9.75	17.3	78	-0.38	21.8	20.5	56.0
	Organic	84	18.4	2.89	4.44	19.5	76	132	29.1	13.8	146
	Residual	83	35.3	3.41	29.9	51.5	77	-23.3	25.4	-55.3	85.7

*** Q1 = 1st quartile (25th percentile); Q3 = 3rd quartile (75th percentile)**

Table X: Two-way ANOVA of metal concentrations

2-way ANOVA: Metals (P=0.05)

	Cadmium				Copper				Iron			
Test	ER	R	O	Res	ER	R	O	Res	ER	R	O	Res
Month			-	-	▨	▨	▨	▨	▨	▨	▨	▨
Sediment Type	▨		-	-	▨	▨	▨	▨	▨	▨	▨	▨
Month*Type			-	-	▨	▨	▨	▨	▨	▨	▨	

	Manganese				Lead				Zinc			
Test	ER	R	O	Res	ER	R	O	Res	ER	R	O	Res
Month	▨	▨	▨	▨	▨	▨	-	▨	▨	▨	▨	
Sediment Type	▨	▨	▨	▨	▨	▨	-	▨	▨		▨	▨
Month*Type	▨		▨	▨	▨		-	▨	▨	▨	▨	

▨	significant at the 95% confidence level
	not significant at the 95% confidence level
-	no comparison possible

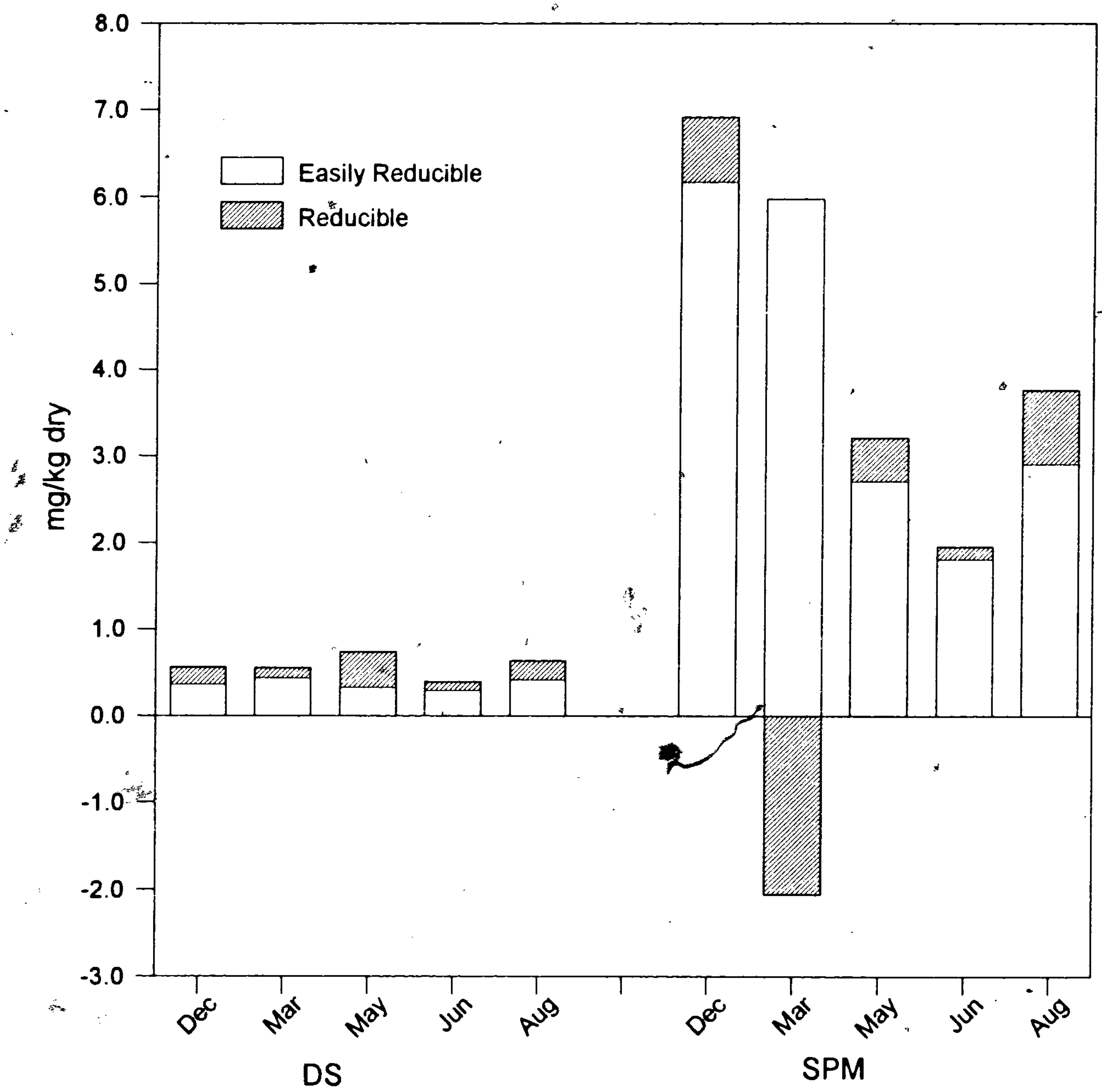
Table XI: Bonferroni t-tests of metal concentrations

SPM vs. DS: Bonferroni t-tests (N=18, P=0.05 experimentwise)

		1994					1995						
Month	**Phase**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**
Cadmium	**ER**	-	-	-	-	▨	-		-	▨	▨	-	▨
	R	-	-	-	-		-		-			-	▨
Copper	**ER**	-	▨	▨	▨	▨	▨			▨		▨	▨
	R		▨		▨	▨	▨	▨	▨	▨	▨	▨	▨
	O	▨	▨	-	▨	▨	▨	▨	▨	▨	▨	▨	▨
	Res		▨		░								
Iron	**ER**	-	▨		▨	▨	▨	▨			░		
	R		▨		▨	▨	▨	▨		▨	▨	▨	▨
	O		▨		▨	▨	▨	▨	▨			▨	▨
	Res					▨				▨	▨		
Lead	**ER**	-	▨	▨	▨	▨	▨			-	-	-	-
	R	-	▨					▨	▨	-	-	-	-
	Res	-	▨				▨			-	-	-	-
Manganese	**ER**	-	▨		▨	▨	▨		▨	▨		▨	▨
	R	▨	▨		▨	▨		▨	▨	▨	▨	▨	▨
	O				▨	▨	▨	▨	▨	▨		▨	▨
	Res						▨		░	▨	▨	▨	
Zinc	**ER**	-	-	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	R	-	-					▨	▨	▨	▨		▨
	O	-	-		▨	▨	▨	▨					
	Res	-	-		░						▨		
		Aug	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**

▨ SPM significantly greater than DS at the 95% confidence level
░ DS significantly greater than SPM at the 95% confidence level
☐ no significant difference between SPM and DS at the 95% confidence level
\- no comparison possible

Figure 4.11 Cadmium concentrations



sediment types. Both easily reducible and reducible cadmium concentrations were not significantly different between months and the month*type interaction was not significant (Table X). Bonferroni t-tests showed significant differences in easily reducible cadmium concentration between the two sediment types as summarized in Table XI.

1.4.2 Copper

Copper concentrations in both sediments were well above detection limits and recovery was possible for all phases (Table IX, Figure 4.12, Appendix 3). Concentrations in all phases but the residual are higher in SPM than in DS (Table IX, with significance summarized in Table XI). Copper concentration in the easily reducible and organic phases show order of magnitude differences between SPM and DS (Figure 4.12). In addition to the notable differences in copper concentrations observed between SPM and DS, a distinct seasonal pattern is evident in SPM concentrations. Copper concentrations in the easily reducible and organic phases of SPM reach maxima of 141 ± 28 and 140 ± 57 mg/kg in January and March, respectively (Appendix 3), consistent with the findings of section 1.3. Copper in these two phases makes up the bulk of the copper present (Figure 4.12). In two instances, concentrations in the reducible extract are below concentrations in the easily reducible, resulting in reducible concentrations below zero. In one instance, copper concentration in the aqua regia digest is less than the sum of the three other phases. Two-way analysis of variance revealed significant effects of month, sediment type, and their interaction terms in all phases (Table X). Bonferroni t-tests indicated that the copper concentrations in SPM are consistently greater than in DS with the exception of the residual phase (Table XI).

1.4.3 Iron

Iron concentrations in both sediments were well above detection limits in all phases (Table IX, Figure 4.13, Appendix 3). Concentrations in all phases are higher in SPM than in DS (Table IX, with significance summarized in Table XI). Iron concentration in SPM is two to four-fold higher than in DS (Figure 4.13). In addition to the notable differences in iron concentrations observed between

Figure 4.12 Copper concentrations

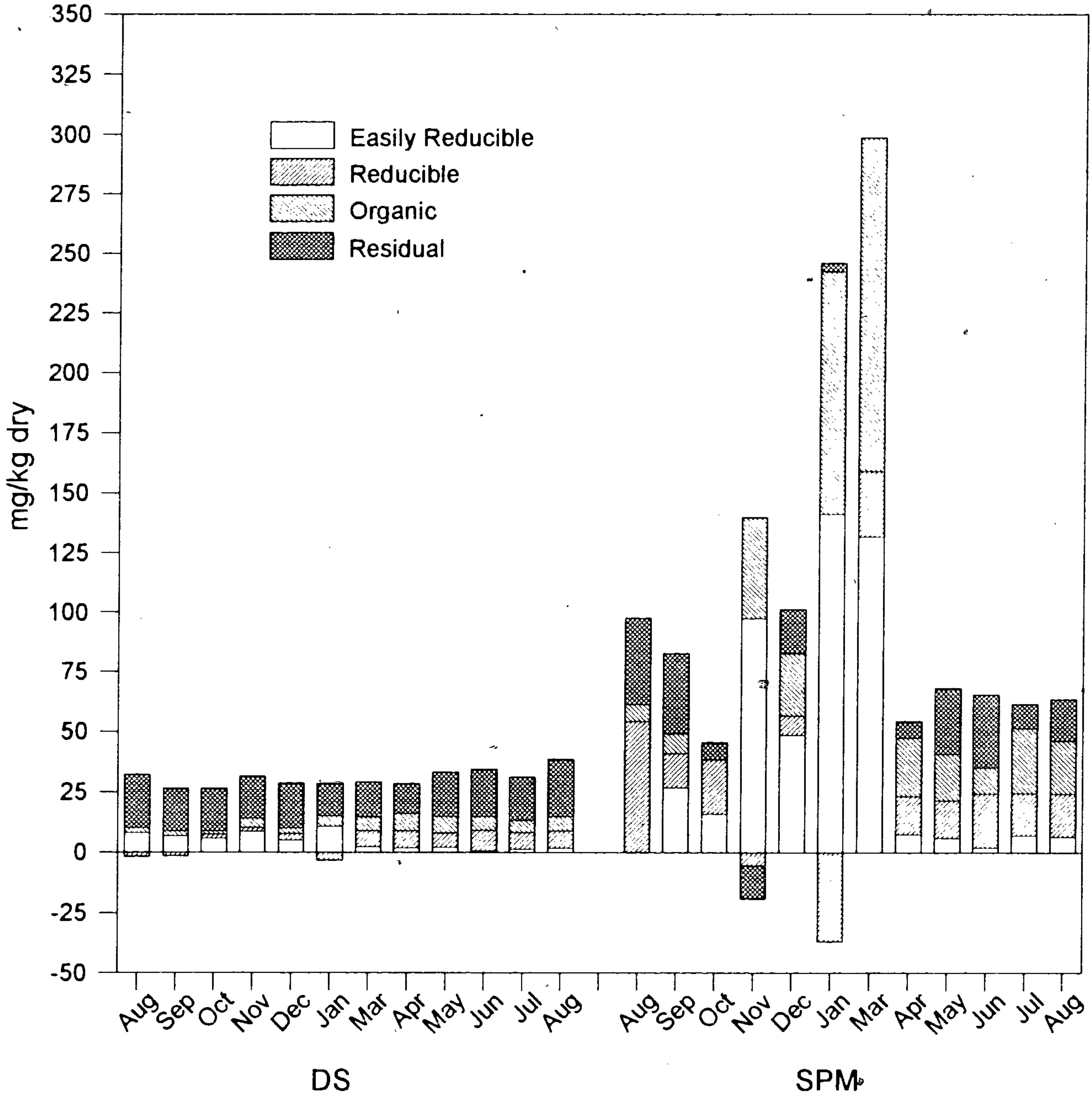
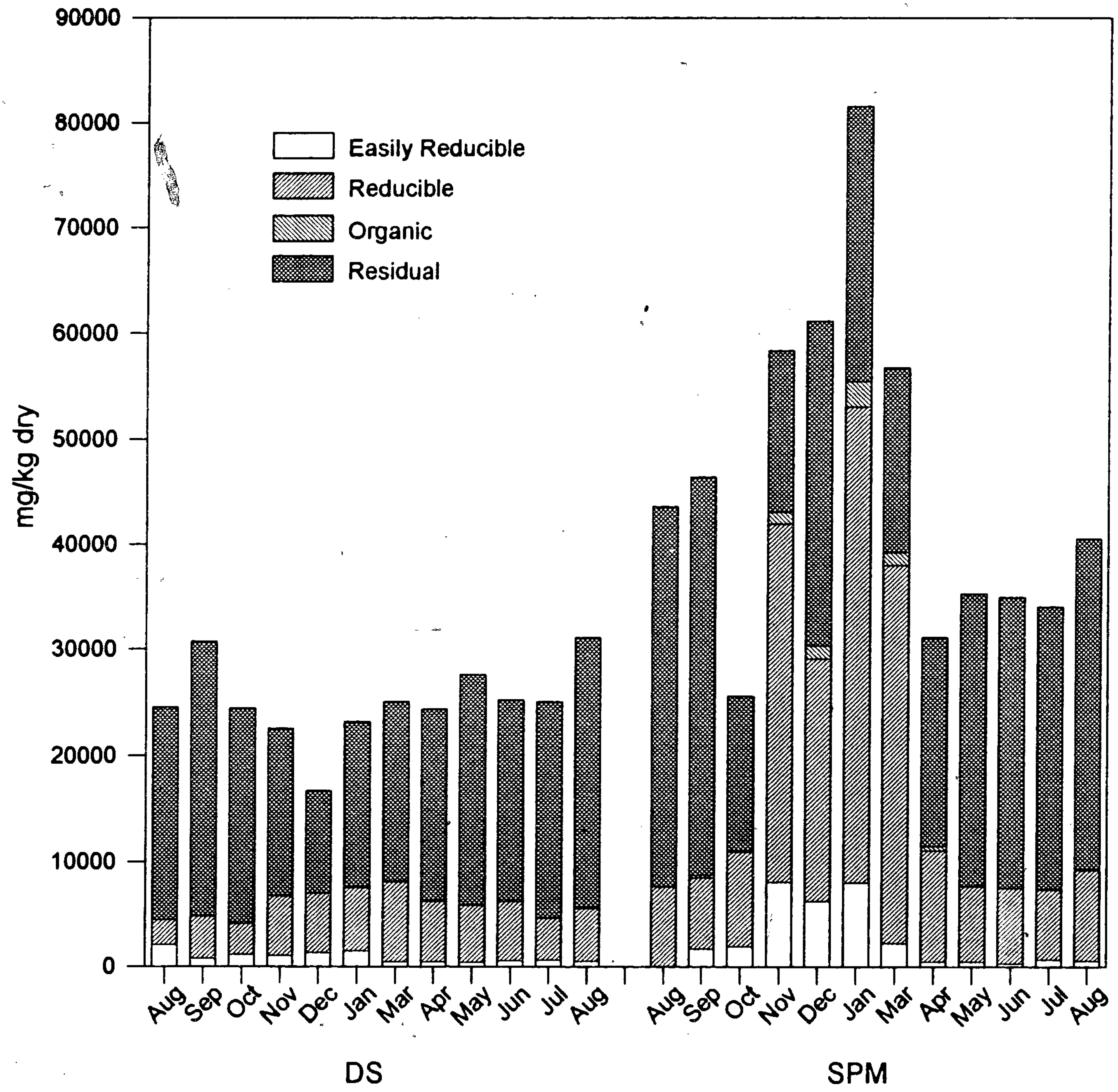


Figure 4.13 Iron concentrations

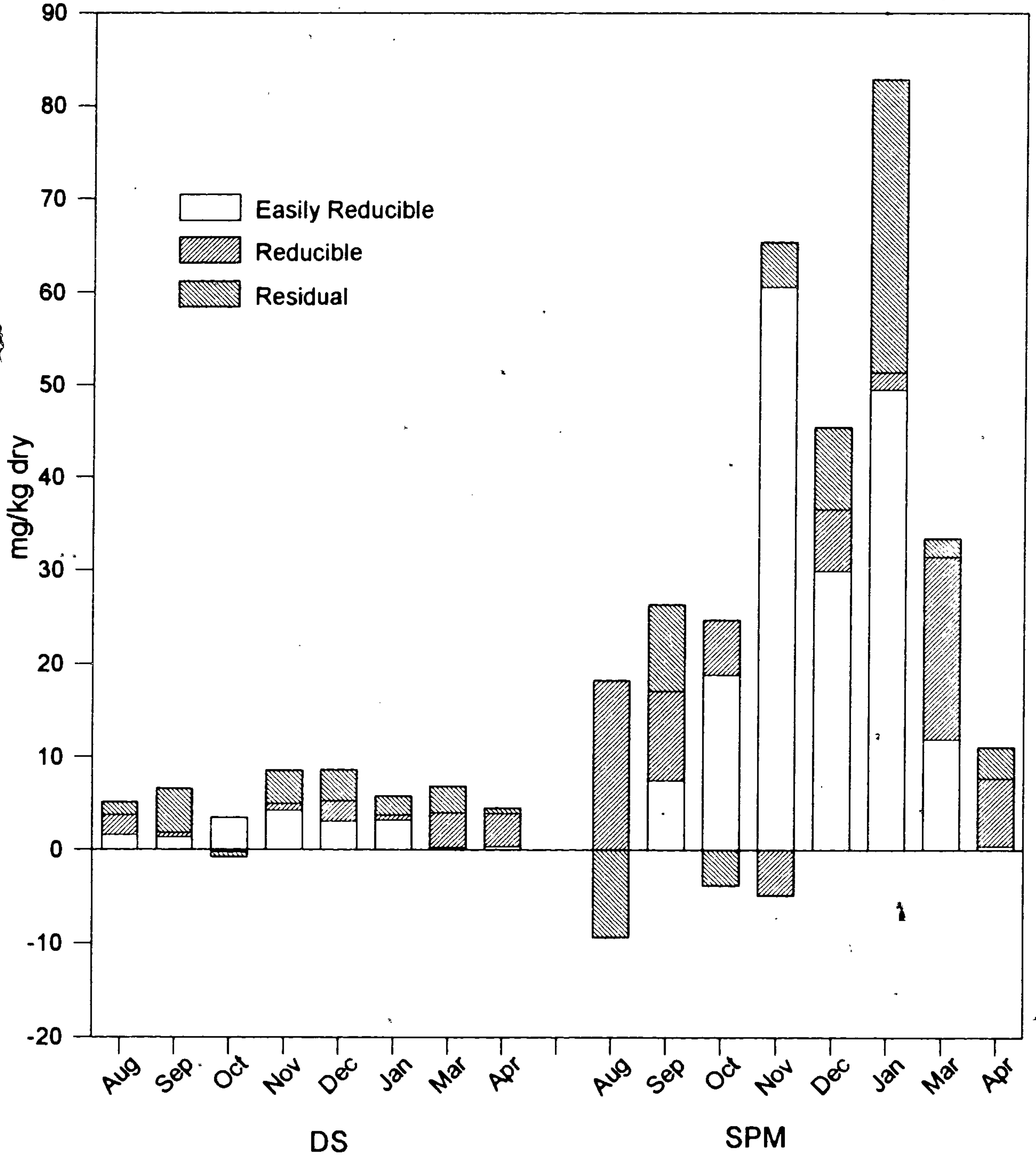


SPM and DS, a distinct seasonal pattern is evident in SPM concentrations. Maxima in SPM concentrations are observed from November through March, which is consistent with the findings of section 1.3. Iron concentrations were highest in the reducible phase, with SPM maxima of 45000 ± 8190 mg/kg in January and DS maxima of 7640 ± 579 mg/kg in March (Appendix 3). Residual iron concentrations in DS and SPM are in the same concentration range (Table X; Appendix 3). Two-way analysis of variance revealed that for all phases except residual, significant effects of month, sediment type, and their interaction terms occur (Table X). In the residual phase, the interaction term is not significant. Bonferroni t-tests indicate that the iron concentrations in SPM are consistently greater than in DS with the exception of the residual phase and, from April through August, the easily reducible phase (Table XI).

1.4.5 Lead

Lead concentrations in the organic phase were always below detection limits; in the easily reducible phase, concentrations were frequently below detection (Appendix 3). Concentrations in all phases are higher in SPM than in DS (Table IX, with significance summarized in Table XI). Order of magnitude differences in concentrations between the two sediments were observed for lead (Figure 4.14). The seasonal pattern observed with other metals and in section 1.3 was apparent with lead. Concentration maxima for lead in SPM were observed from November through March and the differences observed were of a greater magnitude than with other metals (Figure 4.14). Concentrations of lead in the easily reducible phase were found to dominate the total concentrations when concentrations were high in the months September to March. Lead in the easily reducible phase of SPM reached maxima of 61.6 ± 16.1 mg/kg in November, whereas easily reducible lead concentrations in DS reach maxima of 4.3 ± 0.4 mg/kg in November (Appendix 3). As with other metals, the difference between the two sediments is much less pronounced in the residual phase. In one instance lead concentrations in the reducible extract was less than in the easily reducible extract; and in two instances, lead concentrations in the aqua regia extract were less than in the remaining three extracts, resulting in concentration values below zero. Two-way analysis of variance revealed that for the easily reducible and residual phases, significant lead concentration differences occurred for month, sediment type, and their interaction terms (Table X). For the reducible phase, the

Figure 4.14 Lead concentrations

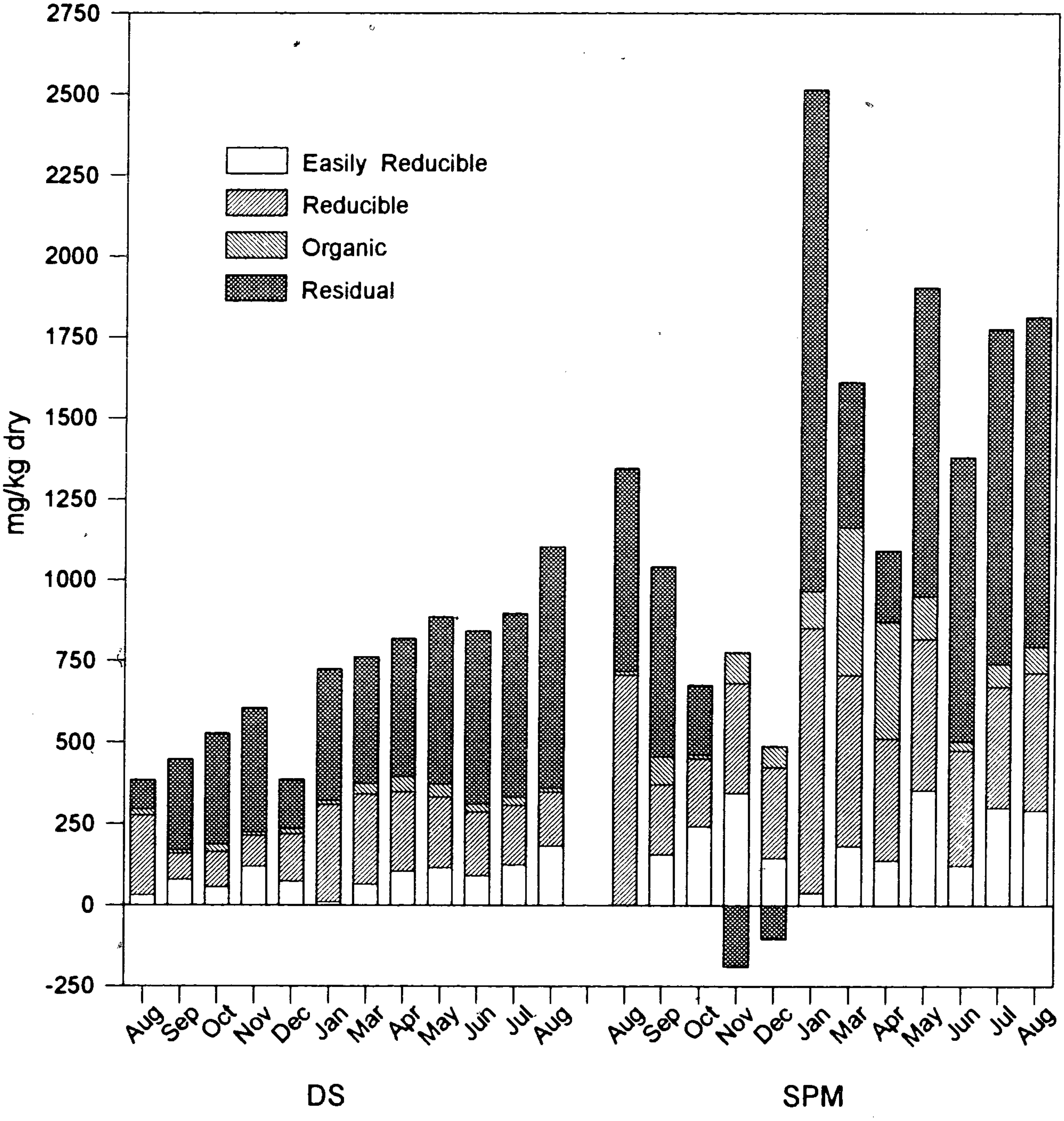


month*type interaction was not significant, while reducible lead concentrations were different among sediment type and month. Table XI summarizes the statistically significant differences between metal concentrations in SPM and DS in the different extracts. Lead concentrations in the easily reducible phase of SPM are consistently greater than in DS. In the reducible and residual phases, such differences are less frequent.

1.4.4 Manganese

Manganese concentrations in both sediments were well above detection limits in all phases (Table IX, Figure 4.15, Appendix 3). Concentrations in all phases are higher in SPM than in DS (Table IX, with significance summarized in Table XI). Two to four-fold differences were found (Figure 4.15). A distinct seasonal pattern in manganese concentrations is evident in SPM concentrations. While concentrations in SPM decreased over the period from August (1994) through December, a maximum follows in January, after which relatively steady concentrations are observed over the rest of the study period. Manganese in the reducible and residual phases dominate total concentration. Manganese concentrations in the reducible phase of SPM reach maxima of 812 ± 130 mg/kg in January, whereas reducible manganese concentrations in DS reach maxima of 301 ± 33 mg/kg in January (Appendix 3). Manganese concentrations in the residual phase of SPM reach maxima of 1550 ± 395 mg/kg in January, whereas residual manganese concentrations in DS reach maxima of 740 ± 77 mg/kg in August (Appendix 3). The difference between the two sediments is somewhat less pronounced in the residual phase. In two instances, manganese concentrations in SPM in the aqua regia digest were lower than in the sum of the remaining digests, resulting in residual manganese concentrations below zero. Two-way analysis of variance revealed that for the easily reducible, organic, and residual phases, significant differences in manganese concentration occurred among month and sediment type and their interaction terms (Table X). The interaction term was not significant for manganese in the organic phase (Table X) Table XI summarizes the statistically significant differences between manganese concentrations in SPM and DS in the different extracts. Manganese concentrations are generally significantly higher in SPM than DS, but this occurred less frequently in the residual phase.

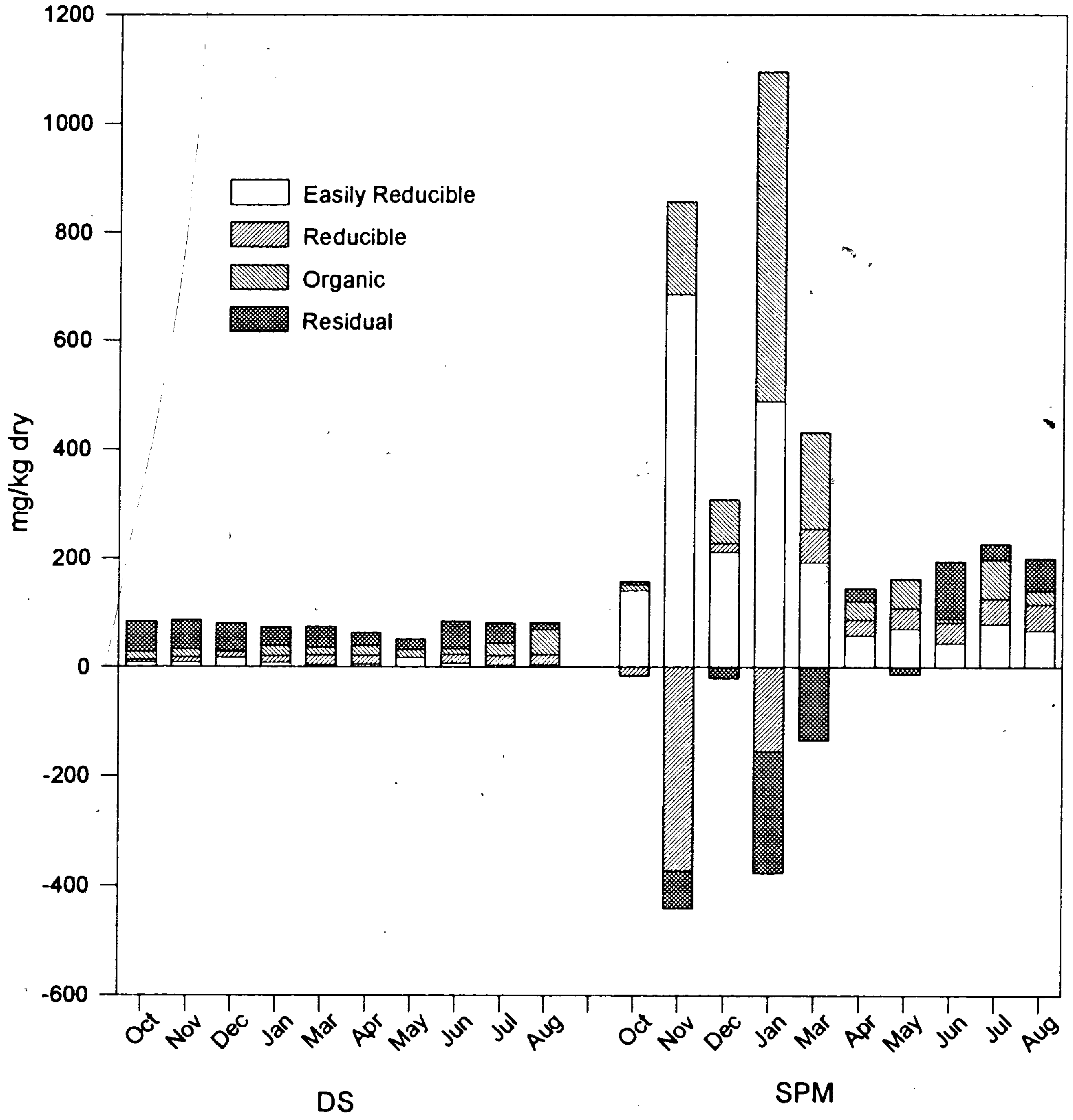
Figure 4.15 Manganese concentrations



1.4.6 Zinc

Zinc concentrations in both sediments were well above detection limits in all phases (Figure 4.16). Concentrations in all phases are higher in SPM than in DS (Table IX, with significance summarized in Table XI). The differences in concentrations between the two sediments were very large for zinc, with order of magnitude differences observed (Figure 4.16). The seasonal pattern observed with other metals and in section 1.3 was apparent with zinc. Concentration maxima for zinc in SPM were observed from November through March and the differences observed were of a greater magnitude than with other metals, with the possible exception of lead (Figure 4.16). Concentrations of zinc in the easily reducible and reducible phases were found to dominate the total concentrations. Zinc in the easily reducible phase of SPM reached maxima of 686 ± 480 mg/kg in November, whereas easily reducible zinc concentrations in DS reach maxima of 17.8 ± 9.7 mg/kg in May (Appendix 3). Zinc in the organic phase reached maxima of 607 ± 160 mg/kg in January, whereas organic zinc concentrations in DS reached maxima of 47.3 ± 19.9 mg/kg in August of 1995. Zinc in the reducible phase of SPM reached maxima of 62.6 ● 16.6 mg/kg in March, whereas reducible zinc concentrations in DS reach maxima of 18.5 ± 2.5 and 18.5 ● 1.6 mg/kg in July and August (Appendix 3). As with other metals, the difference between the two sediments is much less pronounced in the residual phase. In three months (November, January and March), when easily reducible and organic zinc dominated the total concentrations, negative values of reducible zinc and/or residual zinc were recorded (Figure 4.16). On three other occasions negative concentrations of reducible or residual metals were calculated for SPM. Two-way analysis of variance revealed that for the easily reducible and organic phases, significant effects occurred for the month, sediment type, and their interaction terms (Table X). For the reducible phase, sediment type was not significant; for the residual phase, only sediment type was significant. Table XI summarizes the statistically significant differences between metal concentrations in SPM and DS in the different extracts. Zinc concentrations in SPM are always significantly greater than in DS in the easily reducible phase. This was also frequently the case in both reducible and organic phases, but not so in the residual phase.

Figure 4.16 Zinc concentrations



1.5 Metal Partitioning

The partitioning of copper, lead, and zinc between the leachable and residual phases of both SPM and DS of the Fraser River Estuary were determined (Figure 4.17). For copper and zinc, it was further possible to partition the metals among the four phases (easily reducible, reducible, organic and residual) (Figure 4.18).

1.5.1 Partitioning among Leachable and Residual Phases

Intersite differences were calculated for the proportion of leachable metal in both DS and SPM for each of the three metals using arcsine transformed data. In all cases, partitioning was not significantly different among the sites ($P > 0.05$). The proportion data were therefore pooled and two-way ANOVA performed (month, sediment type, and interaction; Table XII) with replicates averaged. This analysis indicates that more copper and zinc are present in leachable phases in SPM than in DS.

Table XII: Two-way ANOVA of partitioning among leachable and residual phases

Metal		*df*	*F*	*P*
Copper *N=70*	*Month*	10	4.02	0.0005
	Type	1	90.59	0.0001
	*Month*Type*	10	1.76	0.0939
Lead *N=66*	*Month*	10	1.90	0.0717
	Type	1	3.09	0.0857
	*Month*Type*	10	1.96	0.0623
Zinc *N=56*	*Month*	9	22.05	0.0621
	Type	1	29.92	0.0001
	*Month*Type*	9	2.23	0.0423

Figure 4.17 Partitioning of copper, lead and zinc between leachable and residual phases

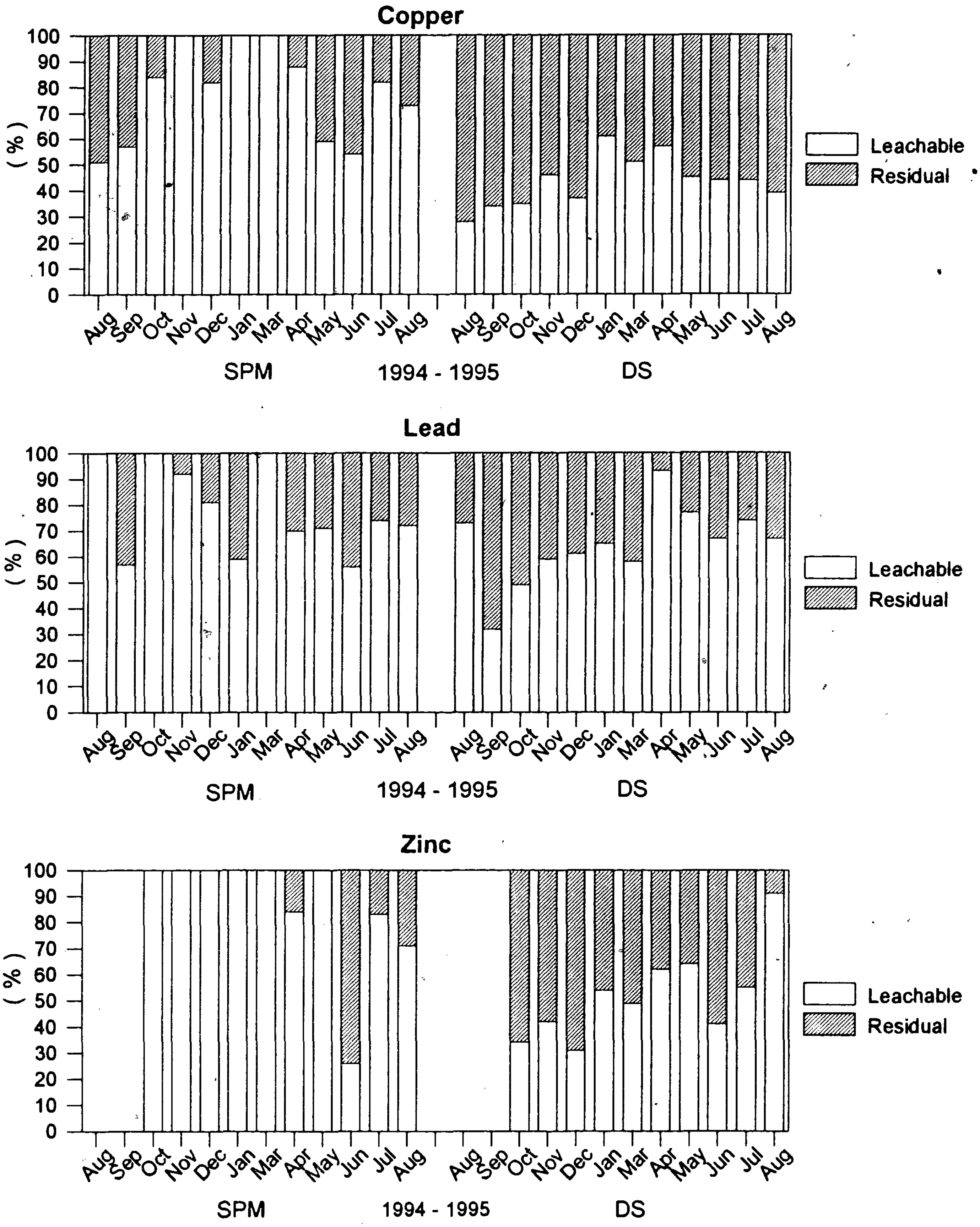
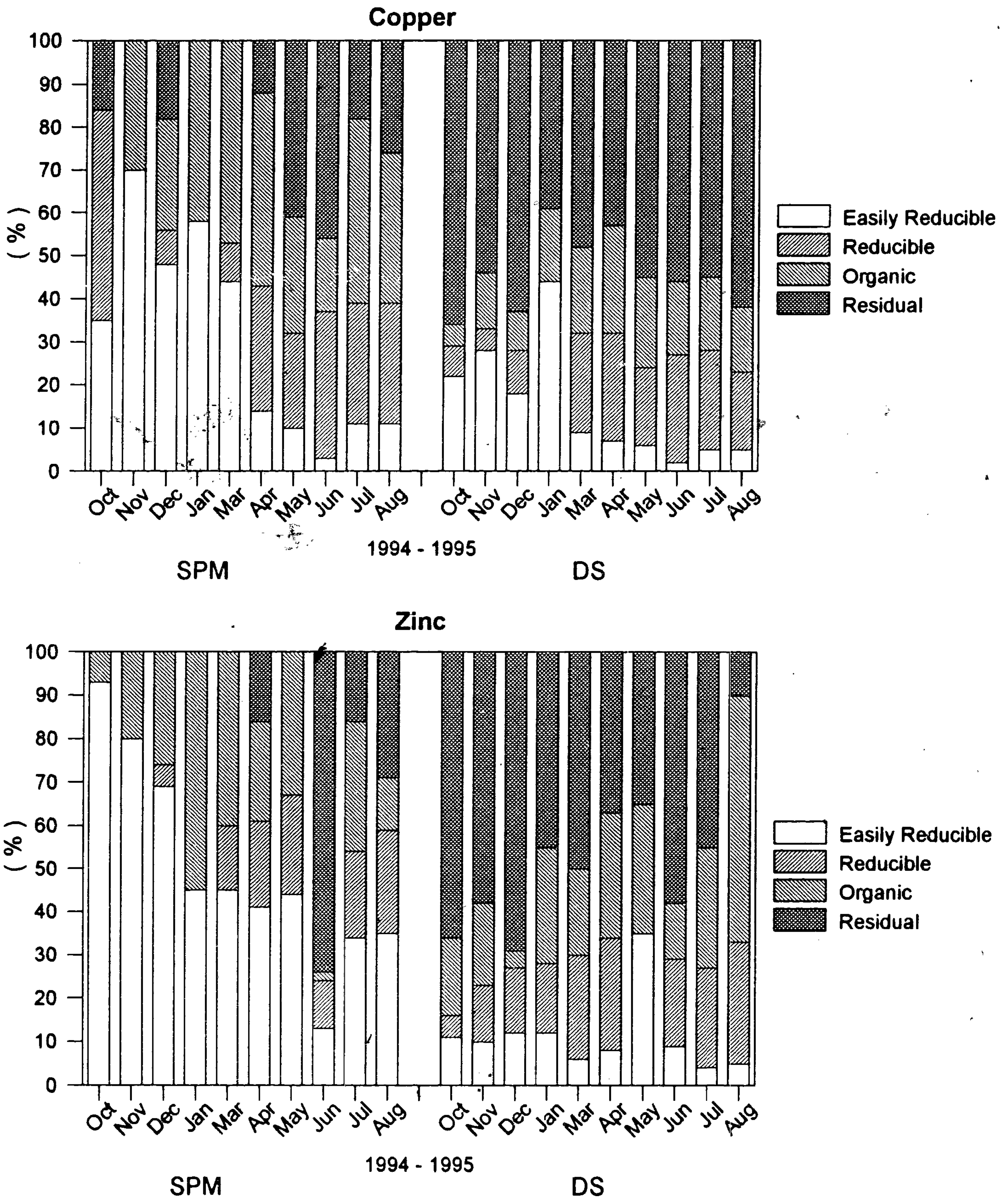


Figure 4.18 Partitioning of copper and zinc in four phases



ANOVA with multiple contrasts (Tukey) was subsequently employed to determine if differences in partitioning between leachable and residual occurred among different months, and if so, which months. These contrasts were performed for each sediment type. Copper partitioning was significantly different between months for both DS (N=34, F=3.07, P=0.0127) and SPM (N=36, F=3.09, P=0.0107). In both cases, multiple contrasts were not sufficiently powerful to determine which months differed. Lead partitioning among the leachable and residual phases was significantly different between months in DS (N=34, F=2.43, P=.0379), but not in SPM (N=32, F=1.60, P=0.1757). Tukey's multiple contrasts did not reveal any consistent differences between months. Zinc partitioning among the leachable and residual phases was significantly different between months in SPM (N=28, F=2.83, P=0.0289), but not in DS (N=28, F=1.54, P=0.2083). However, for SPM, multiple contrasts were not sufficiently powerful to determine which months differed.

Bonferroni t-testing indicated that the leachable proportion of copper was greater in SPM than DS in the months of April, August, December, January, March, and November. As noted in Table XIV, the effects of sediment type were not significant for lead. For Zinc, December, January, March and November had higher proportions of leachable Zn in SPM than DS.

1.5.2 Partitioning among the Easily Reducible, Reducible and Organic Phases

For copper and zinc, it was further possible to analyze partitioning among three phases (easily reducible, reducible, and organic). The analyses used are the same as those used for partitioning between leachable and residual phases. Intersite differences were calculated for the proportion of metal in each phase in both DS and SPM using arcsine transformed data. For copper, in all cases partitioning was not significantly different among the sites ($P > 0.05$). The data were pooled and a two-way ANOVA performed (month, sediment type, interaction; Table XIII).

Table XIII: Two-way ANOVA of copper partitioning among the three phases

Metal		*df*	*F*	*P*
ER Cu *N=63*	*Month*	10	19.31	0.0001
	Type	1	15.35	0.0003
	*Month*Type*	8	1.39	0.2267
R Cu *N=63*	*Month*	10	5.92	0.0001
	Type	1	3.63	0.0633
	*Month*Type*	8	0.86	0.5570
O Cu *N=63*	*Month*	10	12.03	0.0001
	Type	1	56.93	0.0001
	*Month*Type*	8	1.96	0.0751

ANOVA with multiple contrasts (Tukey) was subsequently employed to determine if differences in the partitioning among the three phases occurred among different months. These contrasts were performed by sediment type. For copper in the easily reducible phase, the proportions present were significantly different between months in both the DS (N=27, F=19.66, P=0.0001) and SPM (N=36, F=9.74, P=0.0001). For copper in the reducible phase, the proportions present were significantly different between months in both the DS (N=27, F=10.42, P=0.0001) and SPM (N=36, F=2.94, P=0.0139). For copper in the organic phase, the proportions present were significantly different between months in SPM (N=36, F=13.46, P=0.0001) but not in DS (N=27, F=1.69, P=0.1700). In all the above cases, Tukey's multiple contrasts revealed no consistent patterns in the differences between months.

The proportion of easily reducible copper is significantly greater in SPM than DS in December and January, while there are no significant differences in other months (Bonferroni t-tests, P=0.05 experimentwise). For reducible copper, the effect of type is not significant (Table XIII). The proportion of organic copper in SPM is significantly greater than DS in August, January, July, March, and May, while there are no significant differences in other months (Bonferroni t-tests, P=0.05 experimentwise).

For zinc, in all cases partitioning was not significantly different among the sites (P > 0.05). The data were pooled and a two-way ANOVA performed (month, sediment type, interaction; Table XIV).

Table XIV: Two-way ANOVA of zinc partitioning among the three phases

Metal		*df*	*F*	*P*
ER Zn	*Month*	8	3.25	0.0068
N=54	*Type*	1	114.79	0.0001
	*Month*Type*	8	1.64	0.1488
R Zn	*Month*	8	4.07	0.0016
N=54	*Type*	1	6.12	0.0182
	*Month*Type*	8	2.00	0.0747
O Zn	*Month*	8	2.33	0.0399
N=54	*Type*	1	0.12	0.7337
	*Month*Type*	8	1.87	0.0950

ANOVA with multiple contrasts (Tukey) was subsequently employed to determine if differences in the partitioning among the three phases occurred among different months. These contrasts were performed by sediment type. For zinc in the easily reducible phase, the proportions present were significantly different between months in DS (N=27, F=6.20, P=0.0007), but not SPM (N=27, F=1.85, P=0.1319). For zinc in the reducible phase, the proportions present were significantly different between months in SPM (N=27, F=3.21, P=0.0189), but not DS (N=27, F=2.07, P=0.0956). In both cases, Tukey's multiple contrasts revealed no consistent patterns in the differences between months. For zinc in the organic phase, the proportions present were not significantly different between months in either DS (N=27, F=2.44, P=0.0550) or SPM (N=27, F=1.86, P=0.1301).

The proportion of easily reducible zinc is significantly greater in SPM than DS in all months but May. The proportion of reducible zinc is significantly greater in SPM than DS in April and January, while there are no significant differences in other months (Bonferroni t-tests, P=0.05 experimentwise). For organic zinc, the effect of type is not significant (Table XIV).

2.0 DISCUSSION

2.1 Trends in Physical Variables

The physical variables of salinity, temperature, and dissolved oxygen (DO) showed strong seasonal trends over the course of the study. pH, considered a master variable in controlling trace metal interactions in freshwater systems (Warren and Zimmerman, 1993) was relatively static over the year of study (Figure 4.1). This is consistent with previous work characterizing estuaries as well-buffered systems (Kennish, 1990). Correlation of dissolved oxygen with temperature; pH with discharge; and turbidity with discharge were observed. The DO-temperature relationship is the result of the higher oxygen capacity of colder waters, while the turbidity-discharge relationship is the result of greater shear forces. The relationship between pH and discharge could be the result of the reduced buffering capacity of river-dominated waters under the high flow condition. However, this relationship, while significant, was not particularly strong (r=0.55). Overall, the physicochemical characteristics of the study area appear to be dominated by seasonal influences, particularly the seasonal effect of discharge; a strong tidal influence on physico-chemistry was not apparent.

2.2 SPM Concentration

The concentration of SPM in the estuary varied substantially over the study interval, with greatest SPM concentrations corresponding to highest river flow (70 mg/L at the midstream site, June 1995). It is usually the first flush as the river rises that carries the greatest concentration of built up particulates (Foster and Charlesworth, 1996). Milliman (1980) notes that 12-30 million tons of sediment are transported annually, with 80% of this occurring during the freshet. During the early freshet, highest concentrations are observed as a pulse of up to approximately 340 mg/L at the Port Mann Bridge in 1969 (Milliman, 1980). The difference in the two values likely stems from the care that was taken in the present study to avoid sampling any recently resuspended material and the fact that the sampling sites were in relatively quiescent areas. Sampling was never carried out in plumes of sediment washing off the mudflats and samples were always taken near the surface. Therefore, the material collected in the present study would effectively represent only the permanently suspended (PS) material. The PS is likely only a subset of the SPM collected in most studies. It has been noted that suspended sand is present in greatest concentrations at low tide and high flow; while suspended silt and clay is remarkably consistent (Milliman, 1980; Ongley et al., 1988). The other cause for this observed difference could be the differences in sampling area. Approximately 40% of the sand (20% of the total load) settles from suspension in the Upper Fraser River estuary, and most of the rest settles prior to reaching the lower estuary (Milliman, 1980). By comparison, Gibbs (1994) noted increasing SPM concentrations proceeding upstream in the Hudson River Estuary, with intermediate concentrations of 40-50 mg/L in the mid-estuarine zone.

The relationship between SPM concentration and discharge is clear, with correlation coefficients in the 0.80 range. Warren and Zimmerman (1994a) found the concentration of SPM to vary directly with river discharge. Interestingly, when considered over the course of the year, SPM and discharge show a hysteresis loop. The hysteresis loop is attributed to seasonal differences in river conditions, biological uptake, source contributions, and storage discharge relationships (Whitfield and Schreier, 1981). Whitfield and Schreier (1981) found that this hysteresis recurs from year to year, but the shape of the loop varies more dramatically from station to station than from year to year. Differences were noted not only in the shape of the hysteresis, but in the direction; in some situations, the loop developed in a clockwise direction, in others counterclockwise, and in others it crosses over, although the clockwise direction was found to be more common (Whitfield and Schreier, 1981). A clockwise pattern would be indicative of seasonal scouring, with diminishing sediment supply as available sediment is moved out of the estuary (i.e., the initial pulse of high flow following the winter picks up more sediment than an equivalent flow in the fall after the suspendable material has been scoured).

No consistent, statistically significant differences in SPM concentrations were observed among the sites. Although the sites are far enough apart that some differences in sediment settling (flocculation), resuspension, and patterns of flow might be expected, these are likely overwhelmed by the high temporal and spatial variability at each site. In addition, Fletcher et al. (1983) believe that particulates are predominantly riverine in origin, thus effecting a degree of consistency among sites along the estuary.

2.3 Sediment Matrix Features of SPM and DS

The sediment matrix features (particle size, organic content, and content of metal oxides) have been found to be of paramount importance in processes of metal transport, release and bioavailability as discussed in Chapter 2. These sediment matrix parameters are considered in the following sections.

2.3.1 Particle Size

Particle size of SPM was remarkably consistent both between sites and at the same sites at different samplings. Mean SPM particle size was generally in the 10-12 µm size range, consistent with previous observations, which note that the SPM population (especially the permanently suspended surface and near surface layers) is uniform (Ongley et al., 1982; Horowitz et al., 1988). Due to limitations in the volume of SPM that could be effectively retrieved, no correlation between particle size and flow was possible. However, the volume of SPM was highly correlated with flow. Thus, a seasonal variation in SPM particle size with flow might be expected as larger particles could be suspended by stronger flows. However, it is evident that there is little difference in particle size between the month of May and August (discharges of 5500 and 3500, respectively). This is consistent with Warren and Zimmerman (1994a), who found that particle size distribution was independent of the SPM concentration and discharge; temperature appeared to control the size distribution through it's control over biological activity. As water temperature increased, particle size increased, possibly due to increased bacterial attachment and flocculation. In addition, they found the majority of the SPM in the Don River (Toronto, Canada) to have particle size in the <10 µm size category. Further, Duinker et al. (1985) found a maximum grain size of 8.5 to 10.7 µm at high SPM concentrations, and a smaller maximum grain size (4.3 to 5.2 µm) at lower SPM concentrations. Particle sizes were especially low during slack water. These particle sizes are somewhat smaller than the mean SPM particle sizes of 10.5 to 12.5 found in the present study. However, particle sizing was only possible when high flows made sufficient material available. Thus, as noted by Duinker et al. (1985), SPM was sized when it was likely to contain a higher proportion of larger particles.

It has been suggested that the fraction of sediment < 62.5 µm is sufficiently fine that almost any flow will suspend it and it is therefore supply limited, while the ≥ 62.5 µm fraction is flow limited (Knighton, 1984). Indeed, Figure 4.7 indicates that only a very small percentage of particles are greater than 40 µm. Given this observation and the fact that this sediment represents material of larger particle size relative to other points in the season, it seems reasonable to conclude that the SPM was comprised material almost exclusively < 62.5 µm. It is also noteworthy that bacteria are a component of SPM and occur in quite uniform size categories. Rao et al. (1993) point to the fact that the 20-40 µm SPM fraction contains more bacteria than other size categories. This fraction is also shown to be the most important size range for contaminant sorption and in their study (on dyes), the most toxic. Based upon this, they suggest that: bacteria are either attracted to and able to concentrate contaminants and/or the extracellular substances secreted by bacteria have an affinity for contaminant molecules. It is likely that the SPM of the Fraser River Estuary contains bacterial populations in the size range of 20-40 µm and bacteria can affect the geochemistry of particles as additional sorption sites and through their metabolic activities.

The particle sizes of DS are somewhat more spatially variable than are the particle sizes of SPM. This general observation is a function of the settling dynamics of the estuary. The middle estuarine site had consistently finer sediments than either the upstream or the downstream sites as indicated by the higher proportion of silt. This is consistent with physical observation of the sediments collected at the three sites. The clay fraction (<2.0 µm) appeared to be relatively uniform in the DS at the three sites. In addition, the clay content of SPM and DS appear to be rather similar. It therefore appears that the major size difference between the two sediment types is that the DS contains from 10 to 50% sand (>62.5 µm), while the SPM contains very little of this material.

2.3.2 Organic Content

Organic contents of both sediments were not significantly different among the three sampling sites. However, two way ANOVA indicated that the effects of month, sediment type and their interaction were all significant (Table IV). The organic content of the SPM showed significant variability over the year, a variability not evident in DS (Figures 4.9 and 4.10). Specifically, the organic content of

SPM was highest in the months of November through May, and was negatively related to discharge. Over the months that the SPM organic content was greatest, it was generally significantly greater than in the DS (Figure 4.9). The static seasonal organic content of DS possibly reflects the continued supply of fresh organic material from the overlying water column (i.e., consistent deposition). DS sampling ensured that only surficial sediment was analyzed. Reasons for the substantial differences in the organic content of SPM and DS are related to particle size. The concentration of aquatic organic matter tends to show a strong positive relationship with decreasing particle size (Forstner and Wittman, 1981; Salomon and Forstner, 1984; Horowitz and Elrick, 1987). In addition, smaller material is believed to be richer in bacteria (Rao et al., 1993), the specific gravity (suspendibility) of organic particles is low, and the terrigenous/mudflat supply of organic material to SPM may be greater than DS. Possible reasons for the noted seasonal pattern are a dilution effect with higher runoff (i.e., relatively constant organic input from upstream sources [i.e., Annacis Island sewage]), and seasonal changes in riverine flow patterns, resulting in the transport of a higher percentage of organic matter to the relatively quiescent south shoreline where the study sites are located. Since particle sizes show little seasonal variability, it would seem that seasonal changes in SPM organic carbon have little to do with particle size. Numerous researchers have observed organic matter maxima in 2 - 6.3 μm size fractions. Changes in flow patterns could result in seasonal differences in organic content given that high flows would be likely to sweep material of low specific gravity through the highly channelized north side of the river, while under lower flows, more of this material could enter the southern channels. The mudflats on the south side of the estuary appear to be the most biologically productive area in the estuary. Thus, if the high organic content is present in this area only in the winter, organisms that have access to it (i.e., filterers) will have available to them a nutritional source of food in a season where food is generally scarce.

In addition to the negative (but not significant) relationships between SPM organic content and discharge, there is a significant negative relationship between temperature and SPM organic content (Table V). While it is difficult to distinguish any temperature effect from a discharge effect, it is interesting to note that bacterial degradative processes would be reduced at reduced temperature. This could result in the remanence of more organic matter at low temperature than at higher temperatures. This also suggests that the organic material present in the SPM is of allochthonous origin since production in the system is lower in the winter. Milliman (1980) found an average of

18% combustible matter in Fraser River SPM and suggested that a large percentage of this material was wood fibre, derived from logging and log storage activities on the river. Organic material occurs as coatings on sediment grains and organic material in discrete particles in aquatic systems (Horowitz and Elrick, 1987), therefore, there is an intimate connection between the size of the particles and the organic matter content. Organic matter itself can occur in a wide variety of size categories, yet it's bacterial complement, and it's interaction with other aquatic particles can be very important in trace metal-particulate interactions in the aquatic environment. Douglas et al. (1993) found a systematic increase in organic carbon and trace elements with decreasing particle size, down to the colloidal fraction.

Ongley et al. (1982), note that seasonal shifts in organic carbon occur over the course of the year, with spring sediments mainly mineral, reflecting active erosion on hydrologically active terrain. Indeed, it is in the spring (April, May and June) that the organic content of the SPM is noted to decrease, presumably due to dilution by terrigenic material. Ongley et al. (1982) found that summer and fall samples reflect abundant organic detritus originating from instream biomass. This observation reflected the hydrological regime of the systems under study, where summer and fall were low flow conditions. This differs from the Fraser River, where sustained high flows are associated with continuous summer snow melt; lower flow occurring only in the winter. It is apparent that the organic content of SPM is generally highest in low flow/low SPM conditions (Duinker et al. 1985; Degens and Illekkot 1985).

2.3.3 Metal Oxide Content

The concentrations of iron and manganese oxides in the sediment were determined by the selective extraction procedures outlined in the methods section. Specifically, iron oxides are operationally defined as the reducible iron (rFe); and manganese oxides are operationally defined as the easily reducible manganese (erMn). The specificity of selective extractions has been supported (Tessier and Campbell, 1988; Belzile et al., 1989; Warren and Zimmerman, 1994b), but has also been criticized (i.e., Kheboian and Bauer, 1987; Nirel and Morel 1990; Tack and Verloo, 1995). Most of the criticism is due to a lack of complete specificity in extracting simple formulated sediments or to resorption of extracted metal to other sediment phases. Regardless of specificity, these methods are a rational way to contrast the geochemical characteristics of SPM and DS.

Reducible Iron

Reducible iron, the operationally defined measure of iron oxide, has been shown to be a key material in the sorption phenomena controlling trace metal particulate interactions in aquatic systems (Luoma and Bryan, 1981; Horowitz and Elrick, 1987; Horowitz, 1991; Bendell-Young and Harvey, 1992; Warren and Zimmerman, 1994b,c). In fact, Horowitz and Elrick (1987) found that amorphous iron oxides appear to exert the greatest control over both particle surface area and trace metal levels.

ANOVA revealed no significant differences in the rFe concentration of sediments among the three sites. Two-way ANOVA on the pooled data indicate the significance of month, the sediment type, and the interaction. The rFe content of both SPM and DS were variable over the course of the study (Figures 4.9 and 4.10), showing the same pattern as observed with organic content of the SPM. Levels of rFe were always greater in SPM than in DS. The rFe concentrations of both sediments were greatest in winter months (low flow) and lowest in summer months (high flow). rFe content of SPM was significantly greater than DS in the months of November through March due to near order of magnitude differences, and in the months of May through August 1995 due to low variability.

Douglas et al. (1993) and Warren and Zimmerman (1994a) found iron oxides of SPM to be independent of particle size, that is, these oxides are present in all size categories. However, Horowitz and Elrick (1987) suggest that the geochemical phase that dominates control over trace element levels may be particle size dependent, and the two are in effect very difficult to distinguish. Thus, iron oxides have a very high surface area, and it is difficult (or impossible) to determine whether it is the scavenging ability of iron oxides or the surface area that determine the geochemical importance. Indeed, Warren and Zimmerman (1994b) note that Fe oxides can be the best predictor of total SPM surface area and a review by Kersten and Forstner (1989) notes that iron oxide maxima are generally observed in the 2-20 μm size range. In the present study, one substrate (SPM) does indeed have smaller particle size and higher iron oxide content. However, any conclusions based on this must also consider the different physico-chemical environments of the two particle types.

Reducible iron in SPM shows a significant negative correlation with discharge, temperature and SPM concentration indicating that as discharge and temperature increases, the reducible iron content of SPM decreases. This could occur for a number of reasons discussed for organic matter. For DS, a significant negative correlation with temperature is observed. This is particularly interesting since this was not observed with either organic matter or easily reducible manganese (Figure 4.10). The seasonal pattern of DS rFe content is identical to that of SPM and could be the result of the settling of fresh SPM to the surficial deposited sediments.

Easily Reducible Manganese

Through the use of selective extraction procedures, it has become apparent that manganese oxides (easily reducible manganese) are important in the sorption of trace metals in aquatic environments (Luoma and Bryan, 1981; Bendell-Young and Harvey, 1992), although some researchers question their importance (i.e., Horowitz and Elrick, 1987). ANOVA revealed no significant differences in the erMn concentration of sediments between the three sites. Two way ANOVA on the pooled data indicate the significance of month, sediment type, and the interaction. The erMn concentration of both SPM and DS were variable over the course of the study (Figure 4.9). Levels in SPM were more variable than in DS and were always higher. Easily reducible manganese in SPM was highly variable over the study, and was frequently, but inconsistently significantly greater than in DS (Figure 4.9). The erMn concentration of DS varied with month with no consistent seasonal pattern.

Higher levels of manganese oxides in SPM could be again related to particle size differences. Kersten and Forstner (1989) note that manganese oxide concentrations are greatest in the < 2 µm size fraction. Reasons for the high variability in easily reducible manganese include the many interactions between biota and manganese oxides. Ongley et al. (1982) found that Mn oxide concentrations in summer suspended solid samples were similar to Mn concentrations in the dominant algal species. Recent research by Sunda and Kieber (1994) has shown that bacteria will coat themselves in manganese oxides, possibly to help them oxidize organic material they otherwise could not make use of. This implies a complex and intimate relationship between bacteria, manganese oxides, and organic matter. Thus, the importance of manganese oxides, noted in the past could also involve bacteria, which are known also to sorb metals. Honeyman and Santschi (1988) point out that current methods assume that the chemical composition of the particle surface (such as coatings and gel layers) is given by the bulk chemical composition of the particle interior. They note that research is needed on the interfacial region and on the role of organisms and non-living organic material in the coupling of metal cycles. The manganese-bacteria relationship and it's importance in metal sorption is a good example of such required research. In addition, the current use of the gasoline additive MMT (methylcyclopentadienyl manganese tricarbonyl) could contribute to manganese oxides, and represents a possible explanation for the temporal variability in the manganese oxide content of SPM.

In deposited sediments, the distribution of manganese is expected to be closely tied to redox and therefore to organic matter distribution (Wangersky, 1986). In the Fraser estuary, redox was always positive in the areas studied. During sediment sampling, redox boundaries were generally observed 4 to 8 cm from the surface. As a result of redox changes with depth and diffusion through pore waters, the surface of DS could be enriched in iron and manganese following diagenetic mobilization, upward diffusion and precipitation (Gobeil et al., 1981).

2.3.4 Relationships between Matrix Features

The matrix features of organic content and reducible iron (rFe) were found to be significantly correlated in SPM, as was rFe and erMn. In DS, there were no significant correlations among these three variables, but rFe was significantly correlated with the percentage of clay-sized particles (<2.0 μm). The correlations between clay and rFe are expected given current geochemical understanding. Geochemical fractions are not confined to certain size classes, and are found as coatings across the entire size spectrum (Warren and Zimmerman, 1993). Thus, the concentration of these phases can be expected to be correlated and under the control of available surface area. The lack of correlation between the matrix features in DS is somewhat surprising, but could be the result of diagenetic processes occurring in these sediments.

2.4 Metal Concentrations

The concentrations of cadmium, copper, lead, and zinc in the four geochemical phases are considered due to their potential biological significance and the dominance of anthropogenic mobilization processes. Iron and manganese are considered more in terms of their influence as metal binding phases (iron and manganese oxides). For example, while iron in the Rhine river was almost 100% of natural origin, more than 80% of Cu, Pb, Zn, and Cd were from anthropogenic sources (Forstner, 1976).

Concentrations of Cd, Cu, Pb, and Zn were found to be higher in SPM than in DS. This difference is most apparent in the easily reducible phase where order of magnitude differences are consistently observed between the concentrations in SPM and DS (Table IX, Figures 4.11 - 4.16). The significance of the SPM vs. DS comparison (Table XI) provides a convenient summary for assessing the frequency of differences in the different metals in different phases. The order of magnitude differences do not hold for the reducible phase, although the reducible copper and lead are approximately 4 times as high in SPM as DS. Reducible cadmium and zinc concentrations are actually lower in SPM than DS. This observation is largely because reducible metal is calculated as the metal extracted in the reducible step minus the easily reducible. In the cases of cadmium and zinc, the easily reducible extract approached or exceeded the reducible. Thus, although the reducible extract from SPM generally contained more metal than DS, actual reducible concentrations can be lower. Organic extracts only contained detectable levels of copper and zinc, and in both cases, these were an order of magnitude greater in SPM than DS. Residual metals were generally similar or lower in SPM than in DS, with the exception of lead which was almost four times higher in SPM. The fact that the scale of metal enrichment in SPM over DS is more pronounced in the "labile" extracts than in the residual phase suggests that the "additional" metal in the SPM may be present as surface coatings (since SPM has a greater surface area). In addition, these particles are surrounded by water, where surface complexation can occur; adsorption of anthropogenic metals could be enriching these sediment particles. That SPM is enriched with metals in the potentially available easily reducible phase is important to any organisms exposed to this material.

Several studies have noted the high metal concentrations associated with suspended particulate matter relative to bottom sediments (Ongley et al., 1982; Van Alsenoy et al., 1993; Gibbs, 1994; Sondi et al., 1994; Santiago et al., 1994; Regnier and Wollast, 1995); and several authors have noted the high concentrations of contaminants in SPM (Douglas et al., 1993; Warren and Zimmerman, 1994b,c). Sondi et al. (1994) found their highest concentrations of metals (Cd, Cu, Cr, Mn, Pb, Ti, Zn) were always in the SPM, while Gibbs (1994) found higher concentrations of Cd, Cu, Co, Cr, Ni, Pb and Zn in SPM than in DS. Gibbs (1994) also found higher levels of these metals in near surface than near bottom SPM. Van Alsenoy (1993) found similar relationships, but found that metals in the < 63 µm size fraction approach those in SPM. However, they found an exception in copper, which was enriched approximately 25 times in SPM over the < 63 µm fraction of deposited sediment, and approximately 65 times over the bulk sediment. Given the common observation of greater metal concentrations in SPM than DS, there is a need to specifically consider the differences in matrix features and phase partitioning underlying the concentration differences.

The differences in metal contents of SPM versus DS and the seasonal pattern of SPM metal content observed in the Fraser River Estuary could be due to one or more of three reasons: particle size effects, concentration of reactive phases, and flow volume/patterns.

Particle size effects

Larger surface areas per unit volume of small particles favours metal sorption. In addition, small particle sizes may be more efficiently digested by extractants. The seasonal variation in SPM metal concentration can also be explained by this mechanism. Several studies show that finer sediments have higher concentrations of iron and manganese oxides, organic matter and metals than do coarse materials (Forstner and Wittman, 1981; Luoma, 1990). Foster and Charlesworth (1996) note that metal concentrations in suspended sediment decrease with increasing discharge. This is believed to occur due to dilution of highly surface reactive small particles with larger particles as turbulence increases with flow. Under low flow conditions, only very small particulates are sampled. At higher flows, small particles are diluted by larger particles thereby decreasing concentrations per volume. Gibbs (1994) attributed greater metal concentrations in SPM than DS to greater surface area, but also to sorption of local metal sources. Particle size alone is unlikely to explain the large seasonal variations observed, since many authors note that the <62.5 µm fraction is evenly distributed, and only permanently suspended material was sampled.

Concentration of reactive phases

This study has shown that the concentrations of organic matter, manganese oxides, and iron oxides are different in SPM and DS. The concentrations of these efficient scavenging phases in a sediment has long been associated with elevated metal concentrations. This mechanism can also explain the differences in SPM metal concentrations over time. Although the mechanism for the seasonal fluctuation in the concentration of these phases is not known, it is clear that the result is a higher metal concentration.

Flow volume/patterns

The variation of SPM metals with flow noted in this study reflects the changes observed in the geochemical characteristics of the SPM (organic matter and oxides; above). In addition, it is important to note that the proportional contribution from contaminated sources (i.e., urban runoff, sewage outfalls) can be much greater in low flow conditions and altered river flow patterns can transport contaminants via different paths than they would take under higher flow conditions. In addition, the majority of sediment movement and deposition in the Fraser River occurs over a short period of time during maximal flow, a large proportion of which is associated with bed load (Milliman, 1980). The occurrence of lower metal content in this sediment than in fine SPM could explain the observed differences between SPM and DS (i.e., Helz et al. 1985; Helz and Sinex, 1986).

The permanently suspended fraction is generally higher in organic carbon which has a low specific gravity, thus keeping it suspended. The metal binding capacities of organic carbon have already been discussed. Ongley (1978 [in Allan, 1979]) found that SPM metals were significantly higher during summer and fall storm events when organic matter constituted a significant proportion of the suspended load. This is analogous to the findings that during low flow (and high organic carbon), metal concentrations are highest in the Fraser. Bodo (1989) found that in the Don River (Toronto, Canada), metal concentrations in SPM tend to decrease as suspended solids concentrations and flow increase and that river particulate material was significantly enriched relative to surficial river sediment with Cu, Hg, Pb, and Zn and is generally comparable to surficial Toronto Harbour bottom material.

2.4.1 Cadmium

The cadmium data set consists of concentrations in the easily reducible and reducible phases of SPM and DS in the months of December, March, May, June and August. The most significant finding is that easily reducible cadmium is generally an order of magnitude greater in SPM than in DS and the difference between the two is significant for each month except March (Figure 4.11, Table XI). Bodo (1989) noted total Cd concentrations 6-9 times greater in SPM than DS, while Gibbs (1994) noted 30 fold differences. The seasonal variation in easily reducible cadmium was much greater in SPM than in DS, reflective of the same observation in the matrix properties. Other researchers have found that the concentration of Cd in the suspended sediments decline with increasing discharge (Salomons and Eysink, 1981).

Maximum mean cadmium concentrations in the easily reducible phase of SPM were in the 6 mg/kg dry wt. range (Appendix 3). By comparison, the British Columbia freshwater lowest effect level (LEL) for total Cd is 0.6 mg/kg and the severe effect level (SEL) is 10 mg/kg (BCMOELP, 1994). Therefore, the easily reducible Cd concentration approaches levels where harmful effects of total Cd are likely to occur upon exposure. Given the difference in biological accessibility between easily reducible and total metal, such concentrations could represent a significant risk to any exposed organisms. For risk over the longer term, it is apparent that exposed organisms will experience seasonally variable cadmium concentrations in a mixture with other metals and contaminants.

2.4.2 Copper

For copper, a complete data set was available for all phases. The most significant finding for copper is that concentrations in the easily reducible and organic phases of SPM are generally an order of magnitude greater than in DS. The concentrations of copper in all phases but residual are significantly greater in SPM than in DS with very few exceptions (see Table XI). Bodo (1989) found total copper concentrations in SPM to be 7-16 times those in DS; while Gibbs (1994) noted 20 fold differences. McKee et al. (1989) found copper to be enriched in surficial "fluff"over DS by 2.8 times in the reducible phase and 7.7 times in the oxidizable phase. In the present study, differences were most apparent in the months of January and March (Figure 4.12), coincident with lowest flows and higher concentrations of suspended particulate organic matter and oxides. Similar observations were made by McKee et al. (1989), who found copper concentrations in the freshly settled surficial "fluff" of Lake Superior to be greater than in the bed sediments. They suggest that diagenetic processes are responsible for metal impoverishment in bottom sediments.

Maximum mean concentrations of copper in the easily reducible and organic phases of SPM reach maximum values in the 140 mg/kg dry wt. range (Appendix 3). By comparison, the British Columbia freshwater lowest effect level (LEL) for total Cu is 16 mg/kg and the severe effect level (SEL) is 110 mg/kg (BCMOELP, 1994). Therefore, the easily reducible and organic concentrations, individually, exceed levels where harmful effects of total Cu are likely to occur upon exposure. Given the difference in biological accessibility between easily reducible and organic metals versus total metal, such concentrations could represent a significant risk to any exposed organisms. For risk over the longer term, it is apparent that exposed organisms will experience seasonally variable copper concentrations in a mixture with other metals and contaminants.

2.4.3 Iron

A complete data set was available for iron, and the geochemically important fraction of iron has already been discussed in section 2.3.3. It is of some interest, however that the concentrations of iron are also greater in SPM than in DS. It is evident that iron concentrations in SPM are generally greater than in DS. As with Cd and Cu, the differences are most pronounced in the months of November through March, the months of low river flow (Figure 4.13). This has been observed by other researchers. For example, Carpenter et al. (1975) found that total Fe and Mn concentrations in "solids" were highest during the winter months in the Susquehanna River. Wangersky (1986) notes that organic material plays an important role in the iron distribution of estuaries as a particulate scavenging surface. The iron concentrations in SPM and DS are consistent with the pattern of organic matter observed (Section 1.3.2).

2.4.4 Lead

The lead data set was somewhat smaller than other metals (except Cd) due to concentrations near the limits of analytical detection via FAAS. No organic lead was detectable and easily reducible lead was undetectable from May through August. As with other metals, the most significant finding for lead is that concentrations in the easily reducible phase are significantly greater in SPM than DS with very few exceptions (Table XI). Such differences are much less common in the reducible and residual phases (Table XI). In the easily reducible phase, lead concentrations are generally an order of magnitude greater in SPM than DS. For both reducible and residual lead, concentrations in SPM are generally approximately four times greater in SPM than DS. Bodo (1989) found total lead concentrations in SPM to be 7-15 times those in DS; while Gibbs (1994) noted 10-15 fold differences. McKee et al. (1989) found lead to be enriched in surficial "fluff"over DS by 20 times in the reducible phase and 19 times in the oxidizable phase. In this study, differences were most apparent in the months of November through March (Figure 4.14), coincident with lower flows and higher concentrations of suspended particulate organic matter and oxides. McKee et al. (1989) also found significant differences in lead concentrations of surficial "fluff" and DS, which they suggest is due to loss from the organic matter and oxide phases during sediment burial. The fourfold greater residual lead concentration in SPM than DS is an interesting but uninterpretable observation, since the lithogenous fraction of the particles should be similar.

Maximum mean concentrations of lead in the easily reducible phase of SPM reach values in the 60 mg/kg dry wt. range (Appendix 3). By comparison, the British Columbia freshwater lowest effect level (LEL) for total Pb is 31 mg/kg and the severe effect level (SEL) is 250 mg/kg (BCMOELP, 1994). Therefore, the easily reducible concentration is in the range where effects begin to occur upon exposure. Given the difference in accessibility between easily reducible versus total metal, such concentrations could represent a significant risk to any exposed organisms. For risk over the longer term, it is apparent that exposed organisms will experience seasonally variable lead concentrations in a mixture with other metals and contaminants.

2.4.5 Manganese

A complete data set was available for manganese, and the geochemically important fraction of manganese has already been discussed in section 2.3.3. It is of some interest, however that the concentrations of manganese are also greater in SPM than in DS, although high variability is observed as noted in section 2.3.3. It is evident that the significant differences in manganese concentrations between SPM and DS are consistent with other metals (Table XI). Over most months, there is no significant difference in residual manganese in the two sediments. A seasonal pattern of SPM manganese similar to that observed with the other metals is difficult to discern. Previous work (McKee, 1989) suggests that differences in concentration of manganese in DS and surficial "fluff" could be due to diagenetic mobilization of manganese. Indeed, the alteration of manganese oxides is an important diagenetic process.

It is of some interest that the gasoline additive MMT (methylcyclopentadienyl manganese tricarbonyl) could be a major source of manganese to the aquatic environment. This relatively new additive could be a factor contributing to observed differences in SPM and DS manganese concentrations, and could be contributing to the very erratic seasonal SPM manganese pattern (as observed with manganese oxides), with implications upon metal-particle interactions.

2.4.6 Zinc

For zinc, a complete data set was available for all phases. The most significant finding for zinc is that concentrations in the easily reducible phase of SPM is generally 20 times greater than in DS; while concentrations in the organic phase are generally almost an order of magnitude greater in SPM than DS. The concentrations of zinc in the easily reducible and organic phases are significantly greater in SPM than in DS with very few exceptions (see Table XI). Bodo (1989) found total zinc concentrations in SPM to be 8-12 times those in DS; while Gibbs (1994) noted 10-15 fold differences. McKee et al. (1989) found copper to be enriched in surficial "fluff"over DS by 3.7 times in the reducible phase and 1.8 times in the oxidizable phase. In the present study, differences were most apparent in the months of November through March (Figure 4.16), coincident with lowest flows and higher concentrations of suspended particulate organic matter and oxides. The concentrations of zinc in both the reducible and residual phases of SPM are generally either very low or negative, indicating that the bulk of zinc is present in the easily reducible and organic phases as is evident in Figure 4.16. Concentration differences between SPM and DS have been noted elsewhere. For example, in the Columbia River, Zn desorbable by seawater, although found in suspended sediment (Evans and Cutshall, 1973) apparently does not occur in sediment collected from the river bed (Johnson, 1974).

Maximum concentrations of zinc in the easily reducible and organic phases of SPM reach maximum values in the 600 mg/kg dry wt. range (Appendix 3). By comparison, the British Columbia freshwater lowest effect level (LEL) for total Zn is 120 mg/kg and the severe effect level (SEL) is 820 mg/kg (BCMOELP, 1994). Therefore, the easily reducible and organic concentrations, individually, approach levels where harmful effects of total Zn are likely to occur upon exposure. Given the difference in biological accessibility between easily reducible and organic metals versus total metal, such concentrations could represent a significant risk to any exposed organisms. For risk over the longer term, it is apparent that exposed organisms will experience seasonally variable zinc concentrations in a mixture with other metals and contaminants.

2.5 Metal Partitioning

No intersite differences in the partitioning of copper, lead and zinc among leachable and residual metals were found. The most significant finding is that SPM contains a higher proportion of leachable Cu and Zn than DS. This observation did not hold for Pb; in fact, there were no significant effects of month, sediment type or the interaction term for Pb (Table XII). The implication of the differences in Cu and Zn partitioning in SPM and DS is that environmental exchange and potential bioavailability occur more readily with SPM associated Cu and Zn than with DS associated Cu and Zn. When the order of magnitude concentration differences are considered in conjunction with this observation, it is clear that on a concentration per weight basis, any organism exposed to SPM will be at greater risk of contaminant uptake and possible effects than an organism coming into contact with the same quantity of DS provided the ability to assimilate metal from these two substrates is similar. For all three metals, no consistent differences in partitioning were found related to months of sampling; partitioning was remarkably consistent over the year. This is consistent with Tessier et al. (1980) who found that although both SPM levels and metal concentrations were highly variable in space and time, speciation patterns for each metal were reasonably constant. In addition, the occurrence of significant partitioning differences between the two sediments did not appear to follow a consistent seasonal pattern as observed with matrix constituents and metal concentrations.

Other researchers have noted metal partitioning differences between SPM and DS. Notably, Duinker et al. (1985) also found that more Cu, Fe, Mg, Ca, Pb, and Al leached from surface seston (SPM) than from near bottom seston, suggesting that leachable portions of these elements may be associated with the permanently suspended fraction. Warren and Zimmerman (1994a) found decreased concentrations of leachable cadmium and zinc associated with large particles. Thus, particle size could have an influence over the differences observed in SPM and DS. In addition, it has been suggested that partitioning differences could be reflective of the degree of enrichment of SPM versus DS. For example, Badri and Aston (1983) found more "non-lithogenous" Zn and Pb in a polluted estuary than in a moderately polluted or unpolluted one. Brook and Moore (1988) found that an increase in sediment metal caused by mining activities occurred predominantly in the reducible and oxidizable phases. Sinclair et al. (1989) found that lead and zinc in SPM downstream of sources were 15-16X greater than upstream, with most of the increase occurring in the exchangeable and reducible fractions. Noted differences could also be related to diagenetic processes and associated metal redistribution occurring in deposited sediments. In a similar study, McKee et al. (1989) note a change in partitioning, as copper in the fluff was mostly associated with organic matter, while oxide associated copper became more important in the bed sediment.

The full phase partitioning scheme was possible only for copper and zinc. Once again, no consistent intersite differences emerged. For copper, significant effects of month and type, but not their interaction were found (Table XII). In addition, type was not significant in the reducible phase. For zinc, significant effects of month and type, but not their interaction were found (Table XIV). Additionally, type was not significant in the organic phase.

The significant findings of the full phase partitioning are that higher proportions of copper and zinc partition into the easily reducible phase of SPM than DS. For copper significantly higher proportions are found associated with the organic phase of SPM than DS. For zinc, significantly higher proportions are found associated with the reducible phase of DS than SPM. It is therefore apparent that copper has a higher affinity for organic material than does zinc, and that zinc is present in the easily reducible form (associated with manganese oxides) in higher proportions than is copper. Copper's strong association with organic matter has been observed by many researchers (Hart and Davies, 1977; Tessier et al., 1980; Luoma and Bryan, 1981; Oakley et al., 1981; Bendell-Young and Harvey 1992; Warren and Zimmerman, 1994c). Warren and Zimmerman (1994c), found that the SPM oxide pool outcompetes the SPM organic pool for Cd, Pb, and Zn, but sorbs Cu with the same relative concentration factor as does particulate organic matter. In the present study, copper partitioned as organic ≥ easily reducible > reducible; zinc as easily reducible > organic > reducible. McKee et al. (1989) found copper to partition in the order organic > reducible > easily reducible and zinc as reducible > organic > easily reducible. Warren and Zimmerman (1993) found copper to partitioning in the order organic > leachable > reducible; while zinc partitioned as reducible > organic > leachable. Thus, while some trends are apparent (i.e., copper's affinity for the organic phase and zinc's affinity for reducible phases), partitioning is not identical among different sediments, most likely due to geochemical differences. Increased reducible zinc was observed with an increase in small particles (Warren and Zimmerman, 1994a). Indeed, numerous researchers have found zinc to be predominantly associated with the easily reducible and reducible phases (Tessier et al., 1980;

Salomons and Forstner, 1984; Sinclair et al., 1989). Similar to the partitioning of Cu and Zn among leachable and residual phases, no consistent seasonal influence is apparent in the differences in phase partitioning in the two sediment types.

2.6 Metal Fate

This study has clearly shown that metal concentrations are often an order of magnitude higher in SPM than DS. It is generally accepted that bottom sediment on estuarine mud flats is made up of settled suspended particulates. If this is the case, why are the concentrations not the same? Two mechanisms can account for this, both of which are interesting in terms of metal fate in the Fraser River Estuary.

The first mechanism is associated with sediment transport and deposition. Fine, permanently suspended particulate material as sampled in this study, may only settle due to flocculation in saline water. If this is the case, metal rich SPM will only settle in the areas sampled for a fraction of the year (winter months). During the spring discharge maxima, bedload transport is greatest, possibly contributing sediment of low metal content to the mudflats. Together, these processes can explain the concentration differences in SPM and DS noted in this study. In addition, if this mechanism is shown to be occurring, it would imply high sediment metals in the depositional areas. Santschi et al. (1990) note that fluvial particles are generally deposited in deltaic regions at rates of 1 to several centimetres per year while only millimetres per year are deposited in estuaries. While this is not consistent with Milliman (1980), it suggests that the deltaic front of the Fraser River is a key depositional region. In the Don River, Bodo (1989) observed that while metal concentrations in SPM are much greater than in river DS, the difference was much less when SPM is compared to DS from the settling area in Lake Ontario. The second mechanism involves the release of metals to overlying waters with diagenesis as observed by McKee (1989). Specifically, McKee et al. (1989) found concentrations of copper and lead to decrease with depth over a transition from fine, freshly settled "fluff" to bottom sediments. Their pore water profiles indicated a diffusive flux of these metals from the upper sediments to the overlying water. The authors speculate that the upward fluxes may be nearly as large as the downward flux of bound Cu and Pb, and suggest substantial remobilization of

Cu and Pb is occurring in the sediment column. They suggest that metals released during the decay of organic matter may be the principle source to the pore waters. Indeed, in sediments, manganese reduction can occur via electron transfer from organic carbon and iron reduction can occur by microbial catalysis in the presence of organic matter (Santschi et al., 1990). The redox cycling that occurs with the degradation of organic matter and reduction of metal oxides can affect the fate of many trace metals (Santschi et al., 1990). The occurrence of such processes in the DS of the sites studied herein could also explain the noted metal concentration differences in SPM and DS. Fletcher et al. (1983) believe that particulates (even if returned from the Straight) are predominantly riverine in origin. Thus, alternate sources of estuarine particles cannot be considered a mechanism for the observed differences in SPM and DS metals concentrations.

Both mechanisms are likely operative in determining the concentration differences observed. Grieve and Fletcher (1977) found more dissolved and particulate zinc in the mixing zone of the Fraser River Estuary than in either the adjacent river or sea, and attributed this to internal cycling and entrapment. Such entrapment should also lead to higher DS metal concentrations during periods of settling (i.e., when the sampling site was clearly in the mixing zone as determined by salinity measurements). This was not observed. Gobeil et al. (1981), working in the St. Lawrence Estuary, hypothesize that although the diagenetically enriched upper centimetre of the DS approaches the Mn/Al and Fe/Al ratios of river SPM, this material is swamped by the bulk turbidity zone SPM, therefore there must be a net export of Mn and Fe from the turbidity maximum zone. Similarly, Kennish (1992) notes that although the largest amounts of heavy metals initially accumulate in upper and middle estuary regions, erosion and transport often displace them to the outer estuary or to areas on the continental shelf beyond the estuarine mouth. Gobeil et al. (1981) found that diagenetic mobilization within the rare fine-grained bottom sediments of the turbidity maximum is responsible for changes in Mn and Fe content of particulate matter. The depletion of both Mn and Fe in the SPM and sediment of the upper estuary implies a net seaward escape of diagenetically mobilized metal. Due to the observed differences in SPM and DS concentrations in the Fraser River Estuary, it appears that a net export of metals is occurring, at least to beyond the furthest site at Reifel Island. Working on the Fraser River Delta slope, Luternauer (1975) found that copper, lead, and zinc concentrations in sediments were greater than concentrations on the tidal flats, with an increase in concentration from South to North along the slope. This would indicate that settling of the SPM with high metal loads appears to occur further out to sea. As seen in the present work, in the estuary, SPM metal concentrations are greater than DS. Thomas and Grill (1977) calculate that the 1.2×10^{13} g of SPM discharged by the Fraser during the May to July freshet would release 3.1×10^{8} g of Cu and 1.1×10^{9} g of Zn. This emphasizes that metal-SPM associations are of overwhelming importance in metal transport and distribution even in the Strait of Georgia. In addition, other studies have shown that a significant portion of chemical transport may occur under relatively low flow conditions due to the high trace element concentrations associated with small size fractions (Horowitz, 1991). Thus, it seems likely that the fate of SPM-associated metals is on the delta slope and desorbed in the Strait. This explains why SPM values are higher than any values found in DS; the DS represents typical underburden, with the fine material washing further down the estuary and becoming susceptible to metal desorption.

3.0 REFERENCES

Allan, R.J.. 1979. Sediment-related fluvial transmission of contaminants: Some advances by 1979. Environment Canada Scientific Series No 107. Inland Waters Directorate. 24 pp.

Badri, M.A. and S.R. Aston. 1983. Observations on heavy metal geochemical associations in polluted and non-polluted estuarine sediments. Environ. Pollut. 6: 181-193.

BCMOELP. 1994. Approved and working criteria for water quality - 1994. Table 1b, Approved and working criteria for sediment quality. British Columbia Ministry of Environment, Lands and Parks. February, 1994.

Belzile, N., P. Lecomte and A. Tessier. 1989. Testing readsorption of trace elements during partial chemical extractions of bottom sediments. Environ. Sci. Technol. 23: 1015-1020.

Bendell-Young, L.I. and H. Harvey. 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochim. Cosmochim. Acta. 56: 1175-1186.

Berner, R.A.. 1980. Early diagenesis: a theoretical approach. Princeton Univeristy Press. Princeton. 241 pp.

Bodo, B.A. 1989. Heavy metals in water and suspended particulates from an urban basin impacting Lake Ontario. Sci. Tot. Env. 87/88: 329-344.

Brook, E.J. and J.N. Moore. 1988. Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in bed sediment from the Clark Fork River, Montana, (U.S.A.). Sci. Tot. Env. 76: 247-266.

Carpenter, J.H., W.L. Bradford and W. Grant. 1975. Processes affecting the composition of estuarine waters (HCO_3, Fe, Mn, Zn, Cu, Ni, Cr, Co and Cd). In: Estuarine Research, Volume 1. (L.E. Cronin (Ed.) Academic Press. 188-214.

Degens, E.T. and V. Ittekkot. 1985. Particulate organic carbon: an overview. Mitt. Geol. Paleontol Inst. Univ Hamburg. SCOPE/UNEP Sonderbd 58: 7-27.

Douglas, G.B., R. Beckett and B.T. Hart. 1993. Fractionation and concentration of suspended particulate matter in natural waters. Hydrol. Process. 7: 177-191.

Duinker, J.C., M.T.J Hillebrand, R.F. Nolting and S. Wellershaus. 1985. The river Ems: Processes affecting the behaviour of metals and organochlorines during estuarine mixing. Neth. J. Sea Res. 19(1): 19-29.

Eisma, D.. 1993. Suspended matter in the aquatic environment. Springer Verlag, New York. 299 pp.

Evans, D.W. and N.H. Cutshall. 1973. Effects of ocean water on the soluble-suspended distribution of Columbia River radionuclides. In: Radioactive Contamination of the Marine Environment, IAEA, Vienna. 125-140.

Fletcher, W.K, G.S. Holmes, and A.G. Lewis. 1983. Geochemistry and biological availability of iron and trace elements in the upper Fraser River Estuary. Mar. Chem. 12: 195-217.

Forstner, U.. 1976. Metal concentrations in freshwater sediments - natural background and cultural effects. In: Interactions between Sediments and Freshwater. H.L. Golterman (Ed.). Junk and Pudoc, The Hague. pp. 94-103.

Forstner, U. and G. Wittman. 1981. Metal pollution in the aquatic environment. 2nd revised edition. Springer-Verlag, New York.

Foster, I.D.L. and S.M. Charlesworth. 1996. Heavy metals in the hydrological cycle: trends and explanation. Hydrol. Process. 10: 227-261.

Gibbs, R.J.. 1994. Metals in the sediments along the Hudson River Estuary. Environ. Int. 20(4): 507-516.

Gobeil, C, B. Sundby and N. Silverberg. 1981. Factors influencing particulate matter geochemistry in the St. Lawrence estuary turbidity maximum. Mar. Chem. 10: 123-140.

Grieve, D. and K. Fletcher. 1977. Interactions between zinc and suspended sediments in the Fraser River Estuary, British Columbia. Estuar. Coast. Shelf. Sci. 5: 415-419.

Hart, B.T. and S.H.R. Davies. 1977. Physico-chemical forms of trace metals and the sediment-water interface. In: Interactions between sediemnts and freshwater. H.L. Golterman (Ed.). W. Junk Publishers, The Hague.

Helz, G.R. and S.A. Sinex. 1986. Influence of infrequent floods on the trace metal composition of estuarine sediments. Mar. Chem. 20: 1-.

Helz, G.R., S.A. Sinex, K.L. Ferri and M. Nichols. 1985. Processes controlling Fe, Mn, and Zn in sediments of Northern Chesapeake Bay. Estuar. Coast. Shelf. Sci. 21: 1-.

Honeyman, B.D. and P.H. Santschi. 1988. Metals in aquatic systems: predicting their scavenging residence times from laboratory data remains a challenge. Environ. Sci. Technol. 22(8): 862-871.

Horowitz, A.J.. 1991. A Primer on sediment-trace element chemistry. 2nd Ed. Lewis Publishers Inc.. 136 pp.

Horowitz, A.J.. 1986. Comparison of methods for the concentration of suspended sediment in river water for subsequent chemical analysis. Environ. Sci. Technol. 20: 155-160.

Horowitz, A.J. and K.A. Elrick. 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Applied Geochemistry 2: 437-451.

Johnson, R.G.. 1974. Particulate matter at the sediment:water interface in coastal environments. J. Mar. Res. 32: 313-330.

Kennish, M.J.. 1990. Ecology of estuaries: Volume II, Biological Aspects. CRC Press, Boca Raton. 391p.

Kennish. M.J.. 1992. Ecology of estuaries: Anthropogenic effects. CRC Press Boca Raton.

Kersten, M. and U. Forstner. 1989. Speciation of trace elements in sediments. In: Trace element speciation: Analytical methods and problems. G.E. Batley (Ed.). CRC Press, Boca Raton. 245-317.

Kheboian, C. and C.F. Bauer. 1987. Accuracy of selective extraction procedures for metal speciation in model aquatic systems. Analyt. Chem. 59: 1417-1423.

Knighton, D.. 1984. Fluvial forms and processes. Edward Arnold Publishers. 218pp.

Luoma, S.N.. 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Heavy metals in the marine environment. R.W. Furness and P.S. Rainbow (Eds.). CRC Press, Boca Raton.

Luoma, S.N. and G.W. Bryan . 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Sci. Tot. Env. 17: 165-196.

Luternauer, J.L.. 1975. Fraser Delta sedimentation, Vancouver, British Columbia. Geol. Surv. Can. , Paper 75-1, Part A. pp. 467- 468.

McKee, J.D., T.P. Wilson, D.T. Long and R.M. Owen. 1989. Pore water profiles and early lake diagenesis of Mn, Cu, and Pb in sediments from large lakes. J. Great Lakes Res. 15(1): 68-83.

Milliman, J.D.. 1980. Sedimentation in the Fraser River and it's estuary, Southwestern British Columbia (Canada). Estuar. Coast. Mar. Sci. 10: 609-633.

Nirel, P.M.V. and F.M.M. Morel. 1990. Pitfalls of sequential extractions. Water Research 24 (8): 1055-1056.

Oakley, S.M., P.D. Nelson and K.J. Williamson. 1981. Model of trace metal partition in marine sediments. Environ. Sci. Technol. 15: 474-480.

Ongley, E.D., D.A. Birkholz, D.A., J.H. Carey and M.R. Samioloff. 1988. Is water a relevant sampling medium for toxic chemicals? An alternative environmental sensing strategy. J. Environ. Qual. 17(3): 391-401.

Ongley, E.D., M.C. Bynoe and J.B. Percival. 1982. Physical and geochemical characteristics of suspended solids, Wilton Creek, Ontario. Hydrobiologica 91: 41-57.

Rao, S.S., B.J. Dutka, and C.M. Taylor. 1993. Ecotoxicological implications of fluvial suspended particulates. In: Particulate matter and aquatic contaminants. S.S. Rao (Ed). Lewis Publishers, Boca Raton. pp. 157-167.

Regnier, P. and R. Wollast. 1995. Distribution of trace metals in suspended matter of the Scheldt estuary. Mar. Chem. 43: 3-19.

Salomons. W. and W. Eysink. 1981. Pathways of mud and particulate trace metals from rivers to the southern North Sea. Spec. Publ. Int. Assoc. Sedimentol. 5:429-450.

Salomons, W. and U. Forstner. 1984. Metals in the hydrocycle. Springer Verlag, Berlin.

Santiago, S., R.L Thomas, G. Larbaigt, C. Corvi, D. Rossel, J. Tassadellas, D.J. Gregor, L. McCarthy and J.P. Vernet. 1994. Nutrient, heavy metal and organic pollutant composition of suspended and bed sediments in the Rhone River. Aquat. Sci. 56(3): 220-242.

Santschi, P., P. Hohener, G. Benoit and M. Buchholtz-ten Brink. 1990. Chemical processes at the sediment-water interface. Mar. Chem. 30: 269-315.

Sinclair, P.L., R. Beckett and B.T. Hart. 1989. Trace elements in suspended particulate matter from the Yarra River, Australia. Hydrobiologia 176/177: 239-251.

Sondi, I., M. Juracic, E. Prohic and V. Pravdic. 1994. Particulates and the environmental capacity for trace metals. A small river as a model for a land-sea transfer system: the Rasa River estuary. Sci. Tot. Env. 155: 173-185.

Sunda, W.G. and D.J Kieber. 1994. Oxidation of humic substances by manganese oxides yields low-molecular-weight organic substrates. Nature 367: 62-64.

Tack, F.M.G. and M.G. Verloo. 11995. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. Intern. J. Environ. Anal. Chem. 59: 225-238.

Tessier, A. and P.G.C. Campbell. 1988. Comments on the testing of the accuracy of an extraction procedure for the speciation of particulate trace metals in sediments. Analyt. Chem. 60: 1475-1476.

Tessier, A., P.G.C. Campbell and M. Bisson. 1980. Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). Can. J. Earth Sci. 17: 90-105.

Thomas, D.J. and E.V. Grill. 1977. The effect of exchange reactions between Fraser River sediment and seawater on the dissolved Cu and Zn concentrations in the Straight of Georgia. Estuar. Coast. Mar. Sci. 5: 421-427.

Van Alsenoy, V., P. Bernard and R. Van Grieken. 1993. Elemental concentrations and heavy metal pollution in sediments and suspended matter from the Belgian North Sea and Scheldt estuary. Sci. Tot. Env. 133: 153-181.

Wangersky, P.J.. 1986. Biological control of trace metal residence time and speciation: A review and synthesis. Mar. Chem. 18: 269-297.

Warren, L.A. and A.P. Zimmerman. 1993. Trace metal-suspended particulate matter associations in a fluvial system: Physical and chemical influences. In. Particulate Matter and Aquatic Contaminants. S.S. Rao (Ed.). Lewis Publishers, Ann Arbor.

Warren, L.A. and A.P. Zimmerman. 1994a. Suspended particulate grain size dynamics and their implications for trace metal sorption in the Don River. Aquat. Sci. 56(4): 348-362.

Warren, L.A. and A.P. Zimmerman. 1994b. The importance of surface area in metal sorption by oxides and organic matter in a heterogeneous natural sediment. Applied Geochemistry 9: 245-254.

Warren, L.A. and A.P. Zimmerman. 1994c. Suspended particulate oxides and organic matter interactions in trace metal sorption reactions in a small urban river. Biogeochemistry 23: 21-34.

Whitfield, P.H. and H. Schreier. 1981. Hysteresis in relationships between discharge and water chemistry in the Fraser River basin, British Columbia. Limnol. Oceanogr. 26(6): 1179-1182.

CHAPTER 5: PHYSICAL AND GEOCHEMICAL DESCRIPTORS OF METAL BEHAVIOUR AND CONCENTRATIONS

Chapter 4 has shown that suspended particulate matter and deposited sediment differ geochemically and in their concentrations of trace metals. It has shown that the content of organic matter, metal oxides, and metals differ substantially over the year for SPM. Lastly, chapter 4 indicated that significant differences in the partitioning of metal occurred in SPM and DS. The present chapter addresses factors influencing how metal concentrations are affected by temporal changes in physico-chemical and geochemical characteristics in the Fraser River Estuary. To address this objective, simple correlation, multiple correlation and canonical discriminant analysis were used (see section 3.0 of Chapter 3).

1.0 RESULTS

1.1 Simple Correlation Analysis

Simple correlation analyses are presented in Tables I and II. The sediment matrix and physico-chemical properties included in this analysis are: organic content (LOI), iron oxide (rFe), manganese oxide (erMn), tide, flow, salinity, temperature, dissolved oxygen, pH, and SPM concentration (Table I). Correlations between LOI and the physico-chemical variables and rFe and the physico-chemical variables are found to be stronger for SPM than DS. Specifically, in SPM, LOI is significantly correlated with rFe salinity, temperature, DO and SPM (the concentration of suspended particulate matter at the time of sampling), while no correlations are evident in DS. In SPM, rFe is correlated with LOI, erMn, flow, salinity, temperature, DO and SPM. The limited number of correlations between erMn and the physico-chemical variables are stronger for DS than SPM. Specifically, erMn in DS is correlated with flow and pH. Correlations among the physicochemical variables are also summarized (Table I). Both flow and SPM volume are significantly correlated with all other physico-chemical variables.

Table I: Correlations among the mean matrix and physico-chemical features

N=39	*LOI*	*rFe*	*erMn*	*tide*	*flow*	*sal*	*temp*	*DO*	*pH*	*SPM*
LOI	*									
rFe	-/0.65*	*								
erMn	-	-/0.38	*							
tide	-	-	-	*						
flow	-	- /-.53	0.27/-	-0.39	*					
sal	-/0.36	-/0.38	-	0.32	-0.47	*				
temp	- /-0.77	-0.60/-0.81	-	-	0.56	-0.48	*			
DO	- /0.59	0.42/0.62	-	-	-0.33	-	-0.81	*		
pH	-	-	0.62/0.59	-	0.55	-	-	0.34	*	
SPM	-/-0.36	- /-0.53	-	-0.45	0.77	-0.40	0.47	-0.36	0.46	*

Only correlation coefficients (r) significant at the 95% level of confidence or higher are included; a dash (-) indicates no significant correlation. * DS/SPM

All metals in their respective phases are included in Tables IIa - d. The clearest differences between the two sediment types are apparent in the correlations with easy reducible metals (Table IIa). For all of the metals, concentration is more closely related to the matrix features in SPM than in DS. Salinity is correlated with Cu in DS, but not in SPM. Highest correlations are observed between rFe and concentrations of Cd, Cu, Pb and Zn in the easily reducible phase of SPM (with correlation coefficients of 0.78 to 0.92), while the same is not observed in DS. In addition, flow, temperature, DO and SPM are strongly correlated to easily reducible Cu, Pb and Zn in SPM, while fewer correlations occur in DS. In the reducible phase, the relationships between metal concentrations in SPM and matrix and physico-chemical features are largely uncoupled, and relationships with the matrix features are negative (Table IIb). More significant relationships are observed with reducible Cu and Pb in DS than in SPM. Specifically, reducible Cu in DS is correlated with erMn and a suite of physico-chemical variables, while reducible lead is significantly correlated with rFe, pH, and SPM concentration. Correlations with organically bound metals were only possible for Cu and Zn (Table

Table IIa: Correlations between easily reducible metals and matrix/physico-chemical features

	DS				*SPM*			
	Cd	*Cu*	*Pb*	*Zn*	*Cd*	*Cu*	*Pb*	*Zn*
N	15	37	23	28	15	36	24	30
LOI	-	0.35	0.42	-	0.82	0.47	0.44	-
rFe	-	-	-	-	0.92	0.84	0.79	0.78
erMn	0.54	-	-	-	-	0.50	0.69	0.49
pH	-0.52	-0.46	-	0.39	-	-	-	-0.39
sal	-	0.53	-	-	-	-	-	-
tide	-	-	-	-	-	-	-	-
flow	-	-0.63	-0.35	-	-	-0.46	-0.54	-0.42
temp	-	-	-	-	-	-0.52	-0.58	-0.46
DO	-	-	-	-	-	-	0.48	0.39
SPM	-	-0.47	-	-	-0.65	-0.50	-0.71	-0.50

For Tables IIa - IId, only correlation coefficients (r) significant at the 95% level of confidence or higher are included; a dash (-) indicates no significant correlation

Table IIb: Correlations between reducible metals and matrix/physico-chemical features

	DS				*SPM*			
	Cd	*Cu*	*Pb*	*Zn*	*Cd*	*Cu*	*Pb*	*Zn*
N	15	37	25	28	15	39	27	30
LOI	-	-	-	-	-	-	-	-
rFe	-	-	0.44	-	-0.51	-0.44	-	-0.57
erMn	-	0.39	-	-	-0.46	-0.31	-	-0.37
pH	-	0.56	0.57	-	-	-	-	-
sal	-	-0.46	-	-	-	-0.34	-	-
tide	-	-	-	-	-	-	-	-
flow	-	0.63	-	-	-	-	-	-
temp	-	-	-	-	-	0.43	-	-
DO	-	-	-	-	-	-	-	-
SPM	-	0.48	0.46	-	-	-	-	-

Table IIc: Correlations between organic metals and matrix/physico-chemical features

	DS		*SPM*	
	Cu	*Zn*	*Cu*	*Zn*
N	36	28	36	28
LOI	-	-	0.48	0.51
rFe	0.48	-	0.71	0.77
erMn	-	0.43	0.46	0.45
pH	0.45	-	-	-
sal	-	-	-	-
tide	-0.40	-	-	-
flow	0.43	-	-0.34	-0.54
temp	-	-	-0.45	-0.58
DO	-	-	-	0.43
SPM	0.50	-	-0.39	0.53

Table IId: Correlations between residual metals and matrix/physico-chemical features

	DS			*SPM*		
	Cu	*Pb*	*Zn*	*Cu*	*Pb*	*Zn*
N	36	25	28	35	25	77
LOI	0.33	-	-	-0.37	-	-0.40
rFe	-	-	-	-0.53	-	-0.66
erMn	-	-	-	-	-	-
pH	-	-	-	-	-	-
sal	-	-	-	-	-	-0.41
tide	-	-	-	-	-	-
flow	-	-	-	-	-	0.51
temp	0.40	-	-	-	-	0.54
DO	-0.42	-0.45	-	-	-	-
SPM	-	-	-	-	-	0.55

IIc). As with easily reducible metals, organic concentrations of Cu and Zn are clearly more closely related to matrix features and flow, temperature, DO, and SPM in SPM than in DS. In SPM, highest correlations were observed with rFe, with correlation coefficients of 0.71 for Cu and 0.77 for Zn. In the DS, Cu shows a significant relationship with rFe and a suite of physico-chemical features. In contrast, only erMn was correlated with zinc in the organic phase of DS. Residual metal concentrations are largely uncoupled with any of the matrix and physico-chemical features, although a few weak correlations were observed for residual Cu and Zn in SPM. Notably, correlations with the matrix features are negative.

1.2 Multiple Correlations

Whereas the single correlations provide detailed information on the relationships between metal concentrations in specific extracts, multiple correlation can determine the overall influence of the measured matrix and physico-chemical features upon metal concentrations in their respective geochemical phases. Three multiple correlations were run for each metal. Specifically, a multiple correlation against physico-chemical variables (LOI, rFe, erMn, flow, temp, tide, sal, pH) was run, followed by a multiple correlation against geochemical variables (LOI, rFe and erMn), followed by a multiple correlation against all physico-chemical and geochemical variables. The results of these correlations (correlation coefficients, r) are summarized in Table III. These analyses indicate that the correlation between geochemical variables and easily reducible metals range from 0.82 to 0.95 for SPM, and only 0.38 to 0.73 for DS. A similar relationship is observed with organic Cu and Zn, where correlations of 0.85 for SPM versus 0.39 for DS and 0.80 for SPM versus 0.43 for DS are observed for Cu and Zn, respectively. For reducible and residual metals, no consistent contrasts between the two sediment types are evident. For the most part, correlations observed between metal concentrations and the physico-chemical features are similar in SPM and DS, ranging from 0.41 to 0.88. In both SPM and DS, the correlations between metal concentration and the physico-chemical variables is highest for easily reducible metal and lowest for residual metal. The same is noted for the matrix features alone and for the correlations run with all the measured variables. In SPM, correlation strength decreases in the order easily reducible, organic, reducible and residual.

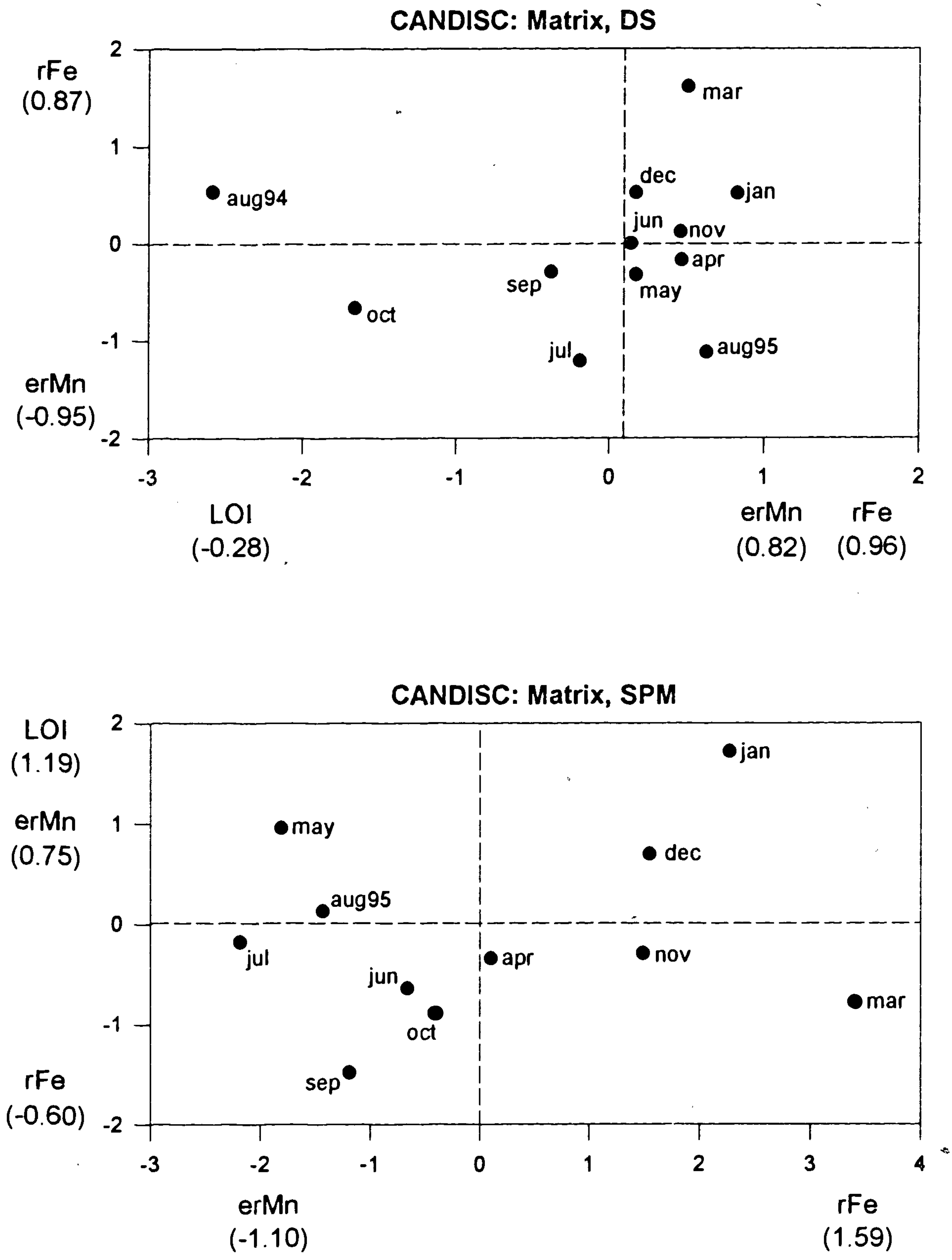
Table III: Comparison of multiple correlations of metal concentrations with physico-chemical and geochemical variables: SPM and DS (N as summarized in Table II)

Metal	*Phase*	*DS*			*SPM*		
		Physico-chem (r)	Geochem (r)	Both (r)	Physico-chem (r)	Geochem (r)	Both (r)
Cd	ER	0.82	0.73	0.92	0.85	0.95	0.97
	R	0.69	0.47	0.80	0.47	0.74	0.90
Cu	ER	0.84	0.39	0.86	0.63	0.85	0.88
	R	0.79	0.47	0.84	0.55	0.50	0.70
	O	0.69	0.59	0.81	0.58	0.72	0.78
	Res	0.51	0.40	0.67	0.43	0.53	0.62
Pb	ER	0.70	0.56	0.78	0.86	0.86	0.95
	R	0.88	0.45	0.90	0.69	0.18	0.69
	Res	0.75	0.34	0.81	0.70	0.32	0.76
Zn	ER	0.68	0.38	0.74	0.58	0.82	0.87
	R	0.62	0.40	0.71	0.41	0.65	0.76
	O	0.43	0.43	0.54	0.70	0.80	0.89
	Res	0.50	0.23	0.51	0.76	0.68	0.85

1.3 Discriminant Analysis

Canonical discriminant analyses determine linear combinations of data that best summarize differences among classes. For the present analyses, the classification variable was taken as month, with the goal of summarizing differences in matrix features (LOI, rFe and erMn) among months (over the seasons of the study period). Results of this procedure are summarized as Figure 5.1. The features that best describe the canonical coefficients are provided on the axes with their weights in brackets, CAN1 on the x axis and CAN2 on the y axis. The values of CAN1 and CAN2 that best describe each month are plotted with the months labelled. For DS (Figure 5.1 top), CAN1 is primarily composed of rFe and erMn (in the positive direction) and LOI (in the negative); CAN2 is

Figure 5.1 Plot of the monthly values of the two canonical variables



primarily rFe (in the positive direction) and erMn (in the negative). This plot indicates that in the winter months, the geochemical composition of DS is dominated by rFe (and erMn; upper right quadrant), while in the summer months it is dominated by erMn (lower quadrants). With SPM (Figure 5.1 bottom), CAN1 is primarily composed of rFe (in the positive direction) and erMn (in the negative); CAN2 is primarily LOI and erMn (in the positive direction) and rFe (in the negative). Similar to the DS observation, this plot demonstrates that in the winter months, geochemical composition of SPM is dominated by rFe (right quadrants), while in the summer months it is less dominated rFe and more by erMn (left quadrants).

1.4 Summary

A summary of the chemical and geochemical "master" variables that appear to exert most control over metal concentrations is provided (Table IV). These variables are summarized from the correlation analysis (section 1.1). Only chemical (pH and salinity) and geochemical (LOI, erMn and rFe) are considered. Physical variables were excluded because while they may control the chemical variables, they are not believed to influence metal partitioning directly.

Table IV: Summary of "master geochemical variables" correlated with metal concentrations

Metal	*Phase*	*DS*	*SPM*
Cd	ER	pH (-), erMn	rFe, LOI
	R	none	rFe (-), erMn (-)
Cu	ER	pH (-), LOI	rFe, erMn
	R	pH, erMn	rFe (-), erMn (-)
	O	rFe, pH	rFe, LOI
	Res	LOI	rFe (-), LOI (-)
Pb	ER	LOI	rFe, erMn
	R	pH, rFe	none
	Res	none	none
Zn	ER	pH	rFe, erMn
	R	pH, rFe	rFe (-), erMn (-)
	O	erMn	rFe, LOI
	Res	none	rFe (-), LOI (-)

2.0 DISCUSSION

The analyses used in this chapter address the relationships between metal concentrations observed in SPM and DS over the course of the study and both physico-chemical conditions and geochemical matrix features. Our current understanding of metal partitioning suggests that the concentration of metal associated with particulates is dependent upon a host of physico-chemical and geochemical factors (Chapter 2). This effort attempts to describe the influences on metal concentrations observed in both SPM and DS of the Fraser River Estuary on the basis of physico-chemical and geochemical features.

2.1 Simple Correlation Analysis

Simple correlations reveal that some of the physical variables are highly correlated. Specifically, dissolved oxygen is adequately explained by temperature and SPM concentrations by flow. However, while these observations are consistent with physico-chemical processes of aquatic systems, correlation does not indicate causation in nature, where a number of unmeasured variables may exist. Such broad based statistical approaches may provide essential information narrowing the focus of more specific studies onto the processes with controlling influence (Luoma, 1983). The observations in this chapter also represent an appropriate means of contrasting the geochemical and physico-chemical influence on metal concentrations in SPM versus DS. In general, the physico-chemical variables of flow, temp, DO and SPM are related over the course of the season. In SPM, organic content (LOI) was related to season (temperature, the concentration of SPM, and DO) and positively related to salinity. This is consistent with increased LOI in winter months, and could be a result of salinity-induced flocculation of organic matter. Reducible iron shows the same correlates as does LOI; it is related to season (flow, temperature, SPM concentration and DO) and positively related to salinity. The seasonal influence is related to the increased iron oxide in winter months observed in chapter 4, with a possible influence of salinity-induced flocculation. The presence of DO is necessary for the formation of iron oxides. Easily reducible manganese is positively related to pH in both SPM and DS and to flow in DS. The role of pH in influencing manganese oxide precipitation and dissolution reactions is well known (Bendell-Young and Harvey, 1992b; Warren and

Zimmerman, 1993; Stumm and Morgan, 1996). In addition, pH is correlated with flow and DO, which contribute to oxide formation.

Relationships between geochemical and physicochemical variables were generally found to be stronger for SPM than for DS (Table I). This observation is consistent with the reactivity of suspended particles in the aquatic environment. SPM is more sensitive to changes in physico-chemical conditions than DS. Related to this reactivity, suspended particles are of higher surface area, contain higher levels of surface phases, and importantly, had a wider variation in properties over the course of the sampling. Easily reducible manganese was an exception in that correlations were better for DS than SPM.

Metals (Cd, Cu, Pb, and Zn) in the easily reducible phase of SPM were more closely correlated to physico-chemical and matrix features than were the metals in DS (Table IIa). Easily reducible metals are associated with manganese oxides and can be mobilized under reducing conditions (Campbell and Tessier, 1987) and conditions of low pH (Bendell-Young and Harvey, 1992a). This study confirms that easily reducible metals are more closely coupled to environmental influences than metals in other phases and that they are more closely coupled in SPM than in DS. Highest correlations were observed between easily reducible metal levels and rFe in SPM. Reducible iron, an operationally defined measure of iron oxides, is widely recognized as an important metal sorption phase (Luoma and Bryan, 1981; Jenne and Zachara, 1987; Horowitz, 1991; Bendell-Young and Harvey 1992b, Warren and Zimmerman 1993). It must also be noted that rFe is related to flow, which is related to all seasonal variables. In the reducible phase, relationships between metal concentrations in SPM and matrix and physico-chemical variables are uncoupled and negative relationships with matrix features are observed in SPM (Table IIb). This unexpected result indicates that when the concentrations of LOI, rFe and erMn are high, there is an increased chance of low (or negative) values in the reducible phase. This is consistent with the observations in chapter 4, where reducible concentrations (concentration in the reducible extract minus concentration in the easily reducible extract) were often negative at the very high matrix concentrations observed during winter months. A greater number of significant relationships are observed with DS but again, no relationship between rFe and reducible Cd, Cu or Pb are observed. Only Cu and Zn were detectable in the organic phase (Table IIc). Similar to the observations with easily reducible metals, Cu and Zn concentrations in the organic phase are more closely related to both matrix features and season (flow, temp, DO, SPM concentration) in SPM than DS. Highest correlations were observed with rFe and LOI. Organic matter (determined by LOI in the present study) is widely recognized as an important metal binding phase (Luoma and Bryan, 1981; Jenne and Zachara, 1987; Sposito, 1987; Horowitz, 1991; Bendell-Young and Harvey 1992b, Warren and Zimmerman 1993), especially for copper (Benjamin and Leckie, 1981; Gardner and Ravenscroft, 1991; Winner 1985; Hering and Morel 1990). Correlations were observed between organic zinc in DS and erMn (Table IIc) whereas for copper, relationships with rFe and a number of physico-chemical factors were observed. Interestingly, no relationship between organic copper in DS and LOI was observed. Residual metals were largely uncoupled from any influence by matrix or physico-chemical features, and again, negative relationships are observed between metals and the concentration of the matrix features in SPM. This is consistent with the consensus that residual metal is non reactive (Tessier et al., 1979; Bendell-Young et al., 1992)..

Luoma and Bryan (1981) have assessed the relationship between selectively extracted metals and operationally defined binding phases. They note relatively weak relationships, although iron extracted with dilute HCl was generally most closely related with extracted metals. Horowitz and Elrick (1987) correlated total metals in sediments with operationally defined binding phases. Since their sediment dataset was obtained from a wide variety of streams and from sieved sediments, correlation coefficients were very high. The strongest relationships were observed with iron oxides (0.83 for Pb to 0.95 for Zn), and LOI (0.83 for Pb to 0.91 for Cu and Zn). They found a lack of significant relationships with manganese oxides and consistently low relationships with total extractable manganese (0.54 for Zn to 0.56 for Cu). However, since a variable component of total metal is biologically inert, the biological significance of such findings is difficult to determine. In addition, different systems with different hydrological and chemical influences, may show different trends. For example, in lake systems, manganese has been implicated as an important metal sorption phase (Bendell-Young and Harvey, 1992). In addition, Horowitz and Elrick (1987) dried their sediments, which can affect metal distributions, particularly those associated with manganese oxides (Jenne and Luoma, 1977). The work of Warren and Zimmerman (1994), although not directly comparable, have shown the relative importance of the binding phases in influencing the distribution of metals among water and the binding phases of suspended particulate matter.

2.2 Multiple Correlations

Multiple correlations provide useful information on the relationship between one variable and a number of other variables. In the current context, simple correlation has provided an effective means of determining relationships between individual measurements. Multiple correlations provide an indication of the overall strength of the relationship between metal concentrations and 1) all measured matrix properties of both SPM and DS, 2) all measured physico-chemical properties at the sample locations, and 3) both sets of variables (Table III). These analyses indicate that correlations between matrix features and metal concentrations in the easily reducible and organic phases are stronger for SPM than DS. These differences are not evident for either reducible or residual metals. In the case of residual metals, this is expected since this metal pool is unreactive. Relationships between metal concentrations and physico-chemical variables are similar among the two metal phases. In both SPM and DS, multiple correlations are strongest between physico-chemical variables and metal concentrations in the easily reducible phase, providing further evidence that this metal pool is most readily influenced by geochemical and physico-chemical factors.

When all matrix and physico-chemical variables are considered, relationships improved, with correlation coefficients of 0.74 to 0.97 for easily reducible metal, 0.69 to 0.90 for reducible, 0.54 to 0.80 for organic, and 0.51 to 0.85 for residual. The overall relative dependence of the metals concentrations upon matrix and physico-chemical features follows the order ER > O > R > Res in SPM and ER > R > O > Res in DS. However, it must be noted that only Cu and Zn were detectable in the organic phase. In terms of SPM/DS differences, both ER and O metals in SPM show higher correlations with matrix features than observed for DS.

2.3 Discriminant Analysis

Canonical discriminant analysis was used to determine the properties of SPM and DS that best characterize the changes occurring over the course of the sampling period (i.e., with season over the course of the year's sampling; Figure 5.1). This analysis indicates that for both SPM and DS, winter months are dominated by reducible iron relative to other months of the year, while in summer months, erMn is relatively more dominant. In both analyses, the winter months (in which time the matrix features and metal concentrations were at their highest) appear in the upper right quadrant, which is characterized by high erMn and high rFe. In chapter 4, it was apparent that reducible iron concentrations of both SPM and DS undergo a significant cycle with maxima occurring during winter months. Seasonal minima are observed during summer months, whereby erMn assumes more importance in explaining variability.

2.4 Summary

From the analyses used in this chapter it was possible to construct a list of "master geochemical variables". In considering these variables, it is noteworthy that LOI and rFe in SPM are correlated as are erMn and pH in both sediment types. In turn, pH is known to influence rFe and erMn (Bendell-Young and Harvey 1992b; Stumm and Morgan, 1996). For SPM, rFe is the dominant master variable, however, LOI and erMn also appear to be important. Organic matter-oxide complexes are believed to occur and enhance oxide sorption of Cu (Warren and Zimmerman, 1994a). Since both iron oxides and organic matter are found to be important in SPM, the same may occur here. Organic matter and oxides have also been found to compete for metals in SPM (Warren and Zimmerman, 1994a), thus it is likely that their influence upon metal concentrations would be related. In contrast, for DS, it appears that pH is the dominant master variable, with rFe, erMn and LOI also important. The importance of pH as a master variable in aquatic systems is well known (Calmano et al., 1993; Warren and Zimmerman, 1993). Horowitz and Elrick (1987) found that amorphous iron oxides exert the greatest control over both surface area and trace metal levels. Overall, they determined geochemical features to affect trace metal concentrations in the following order: amorphous Fe oxide > total extractable Fe > TOC > reactive Fe > %clay > total extractable Mn > Mn oxides. Overall, the results of the present study support the rank of iron oxides (rFe) as the most important variable determining trace metal concentrations. The importance of manganese oxides (erMn) is also supported. However, Horowitz and Elrick (1987) suggest that reactive iron (removed by the same extraction step as Mn oxides) may be the important easily reducible binding phase since it often correlates better with trace elements.

SPM is more closely related to the physical and geochemical features known to influence metal associations and behaviour. In particular, stronger correlations between easily reducible and organic metal concentrations and geochemical matrix features are more evident in SPM than in DS. Therefore, it appears that SPM is an appropriate vector for the study of factors that determine (correlate with) metals; effort in developing an understanding of geochemistry would be well spent studying SPM. The results are consistent with SPM's intimate contact with water and the factors known to influence metals, and the fact that a greater variety of conditions (higher variability and broader representation of geochemical characteristics) exist with SPM than DS. Indeed, SPM displays much more marked spatial and temporal chemical and physical variability than bed sediments (Forstner and Wittman, 1981; Salomons and Forstner, 1984; Ongley et al., 1988; Horowitz et al., 1990).

3.0 REFERENCES

Bendell-Young. L.I. and H.H. Harvey. 1992a. Geochemistry of Mn and Fe in lake sediments in relation to lake acidity. Limnol. Oceanogr. 37(3): 603-613.

Bendell-Young, L.I. and H.H. Harvey. 1992b. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochim. Cosmochim. Acta. 56: 1175-1186.

Bendell-Young, L.I., M. Dutton and F.R. Pick. 1992. Contrasting two methods for determining trace metal partitioning in oxidized lake sediments. Biogeochem. 17: 205-219.

Benjamin, M. and J.O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci. 79: 209-219.

Calmano, W., J. Hong and U. Forstner. 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Wat. Sci. Tech. 28(8-9): 223-235.

Forstner, U. and G. Wittman. 1981. Metal pollution in the aquatic environment. Second revised edition. Springer-Verlag, New York.

Gardner, M. and J. Ravenscroft. The behaviour of copper complexation in rivers and estuaries: two studies in north east England. Chemosphere 23(6): 695-713.

Hering, J.G. and F.M.M. Morel. 1990. The kinetics of trace metal complexation: implications for metal reactivity in natural waters. In: Aquatic chemical kinetics. W. Stumm (Ed.). John Wiley and Sons, New York. 145-171.

Horowitz, A.J.. 1991. A primer on sediment-trace element chemistry. Second Edition, Lewis Publishers, Chelsea, Michigan. 136pp.

Horowitz, A.J. and K.A. Elrick. 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Applied Geochemistry 2: 437-451.

Horowitz, A.J., F.A. Rinella, P. Lamothe, T.L. Miller, T.K. Edwards, R.L. Roche and D.A. Rickert. 1990. Variations in suspended sediment and associated trace element concentrations in selected riverine cross sections. Environ. Sci. Technol. 24: 1313-1320.

Jenne, E.A. and J.M. Zachara. 1987. Factors influencing the sorption of metals. In: Fate and effects of sediment-bound chemicals in aquatic systems. K.L. Dickson, A.W. Maki and W.A. Brungs (Eds.). Pergammon Press, New York. pp. 83-98.

Jenne, E.A. and S.N. Luoma. 1977. Forms of trace elements in soils, sediments and associated waters: an overview of their determination and biological availability. In: Biological implications of metals in the environment. R. Wildung and H. Drucker (Eds.). pp110-143.

Luoma, S.N.. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci. Tot. Env. 28: 1-22.

Luoma, S.N. and G.W. Bryan. 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediment employing chemical extractants. Sci. Tot. Env. 17: 165-196.

Ongley, E., D. Birkholz, J. Carey and M. Samoiloff. 1988. Is water a relevant sampling medium for toxic chemicals? an alternative environmental sensing strategy. J. Environ. Qual. 17: 391-401.

Salomons, W. and U. Forstner. 1984. Metals in the hydrocycle. Springer-Verlag, New York.

Sposito, G.. 1987. Sorption of trace metals by humic materials in soils and natural waters. CRC Crit Rev. Environ. Control. 16(2): 193-229.

Tessier, A. and P.G.C. Campbell. 1987. Partitioning of trace metals in sediments: relationships with bioavailability. Hydrobiol. 149: 43-52.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem. 51(7): 844-851.

Winner. R.W.. 1985. Bioaccumulation and toxicity of copper as affected by interaction between hunic acid and water hardness. Wat. Res. 19: 449-455.

Warren, L.A. and A.P. Zimmerman. 1994. Suspended particulate oxides and organic matter interactions in trace metal sorption reactions in a small urban river. Biogeochem. 23: 21-34.

Warren, L.A. and A.P. Zimmerman. 1993. Trace metal-suspended particulate matter associations in a fluvial system: Physical and chemical influences. In. Particulate Matter and Aquatic Contaminants. S.S. Rao (Ed.). Lewis Publishers, Ann Arbor.

CHAPTER 6: CADMIUM ASSIMILATION FROM SUSPENDED PARTICULATE MATTER AND DEPOSITED SEDIMENT

Chapter 4 has shown that suspended particulate matter and deposited sediment differ geochemically and in their concentration of trace metals. It has also shown that the content of organic matter, metal oxides and metals differ substantially over the year for SPM. Lastly, chapter 4 indicated that significant differences in the partitioning of metals occurred in SPM versus DS. Chapter 5 has demonstrated that the concentrations of metals in the easily reducible and organic phases of SPM are related to the geochemical characteristics of the sediment, particularly the content of iron oxides (rFe), manganese oxides (erMn) and organic matter. In contrast, metal concentrations in deposited sediment appear to be less closely coupled with these geochemical characteristics. This chapter addresses objective 4 outlined in the introduction; how the geochemical characteristics of SPM and DS affect metal (^{109}Cd) assimilation and uptake in estuarine particle consumers (*Protothaca staminea* and *Macoma balthica*).

1.0 RESULTS

To determine the bioavailability of ^{109}Cd, assimilation efficiency and uptake from both SPM and DS were determined. To accurately assess the influence of geochemistry, the two sediments were geochemically characterized and the phase distribution of the spiked metals was assessed. In addition, the sorption/desorption behaviour of the isotopes was monitored throughout the experiments.

1.1 Sediment Geochemistry

Geochemical characteristics of the sediments used in these experiments are provided in Table I. There is no statistically significant difference between the organic content (LOI) of the two sediments (P=0.1432). However, statistically significant differences were found in both the reducible iron and easily reducible manganese content of the two sediments (P=0.0001 and 0.0216, respectively).

Table I: Sediment geochemical characteristics

	SPM (N=5)		*DS (N=3)*	
	Mean	*SE*	*Mean*	*SE*
LOI (%)	6.50	1.29	4.19	0.21
rFe (mg/kg)	12320	478	6545	293
erMn (mg/kg)	418	8	197	35

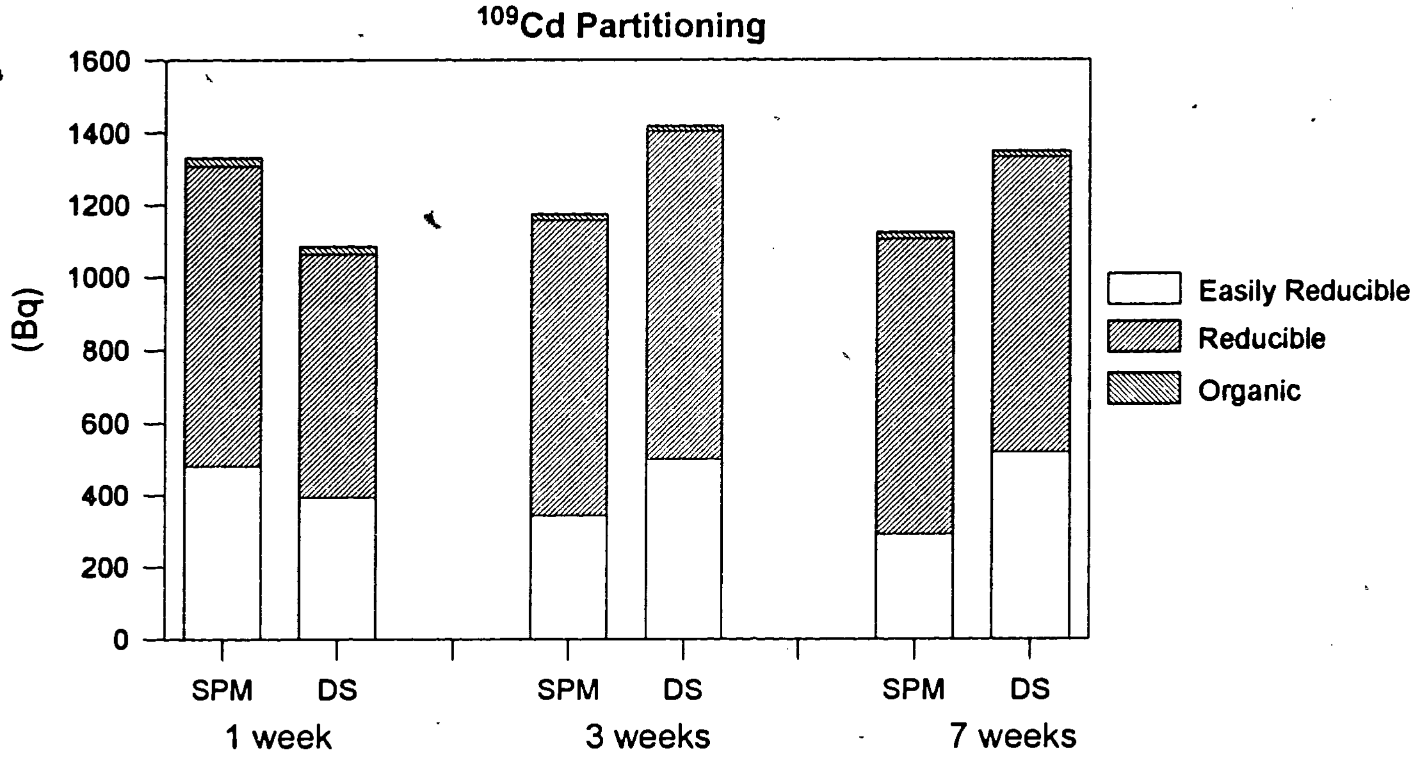
1.2 Isotope Partitioning in SPM and DS

The partitioning of the radioisotopes in SPM and DS following 1 week, 3 weeks, and 7 weeks of equilibration reveal some key differences (Figure 6.1). ^{109}Cd partitioning in the two sediments is not significantly different in any consistent way. However, the partitioning of ^{241}Am reveals a significantly higher proportion of ^{241}Am in the easily reducible phase of DS than in SPM (P=0.000, 0.002, and 0.001 at 1, 3 and 7 weeks, respectively), and significantly higher proportions of ^{241}Am in the reducible (P=0.004, 0.025, and 0.007, respectively) and organic (P=0.005, 0.000, and 0.000, respectively) phases of SPM than DS .

1.3 Isotope Desorption

The desorption of both ^{109}Cd and ^{241}Am following their addition to the aquaria was monitored in each experiment (Figure 6.2). More ^{109}Cd desorbed from DS than from SPM; the differences at all intervals greater than 48 hours were significant at P=0.05 (experimentwise). No statistically significant differences were found in the desorption of ^{241}Am from the two sediments. The partition coefficients (K_d) of the two isotopes in the two sediments were also calculated (Figure 6.3). The partition coefficient for ^{241}Am is much greater than for ^{109}Cd, indicating that ^{241}Am associates much more strongly with the sediment than does ^{109}Cd. For ^{109}Cd, partition coefficients were initially quite

Figure 6.1 Radioisotope partitioning in SPM and DS



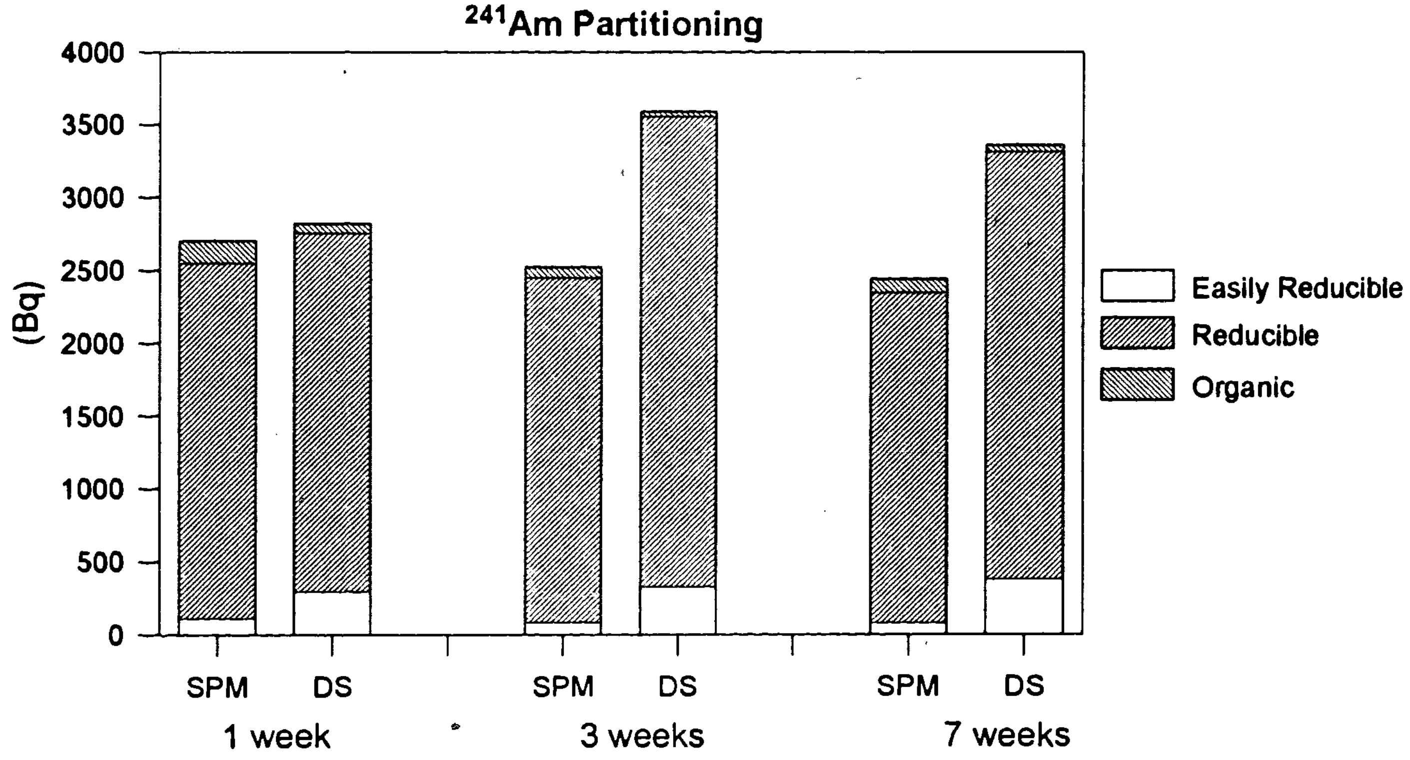


Figure 6.2 Radioisotope desorption from SPM and DS

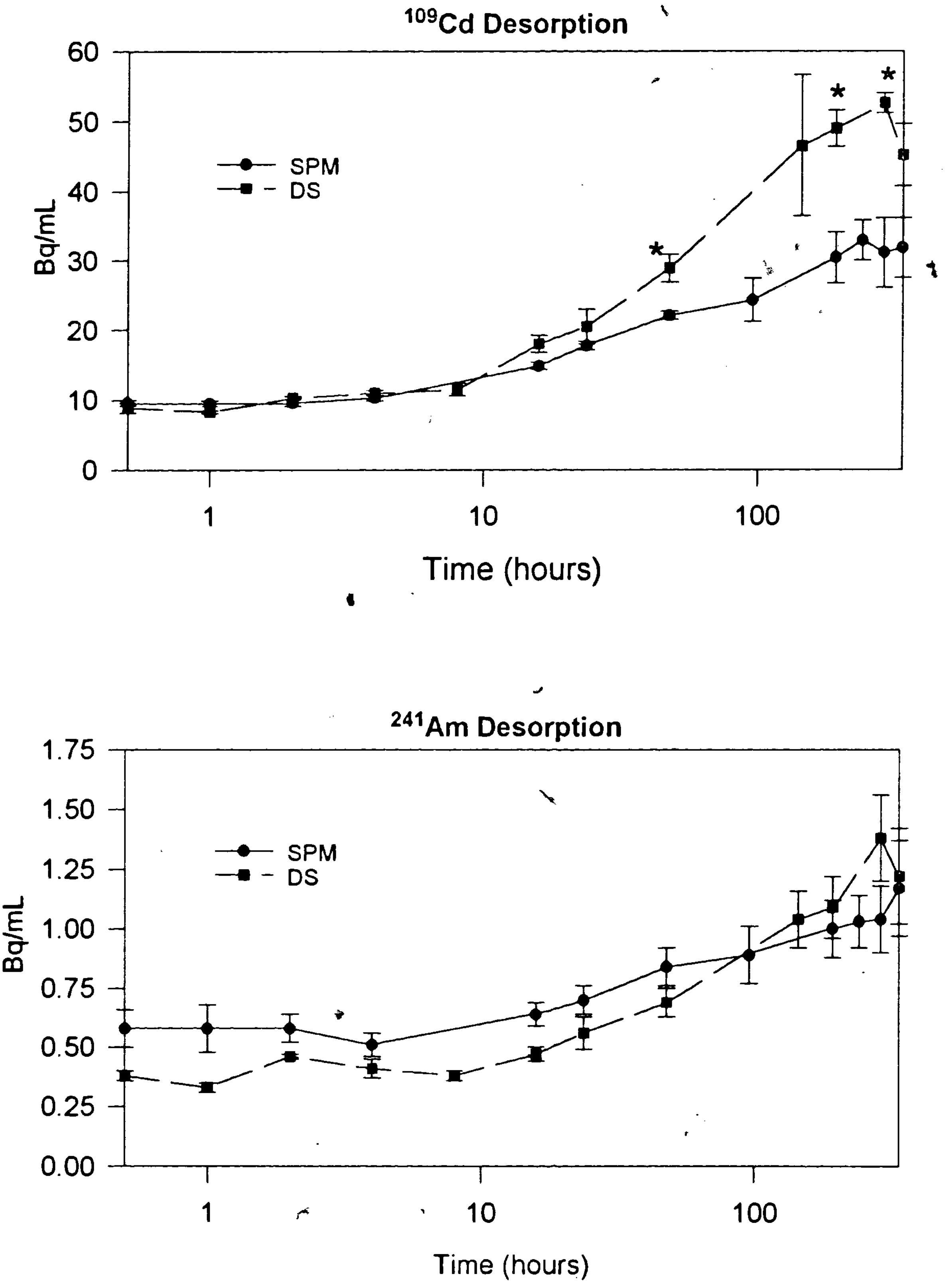
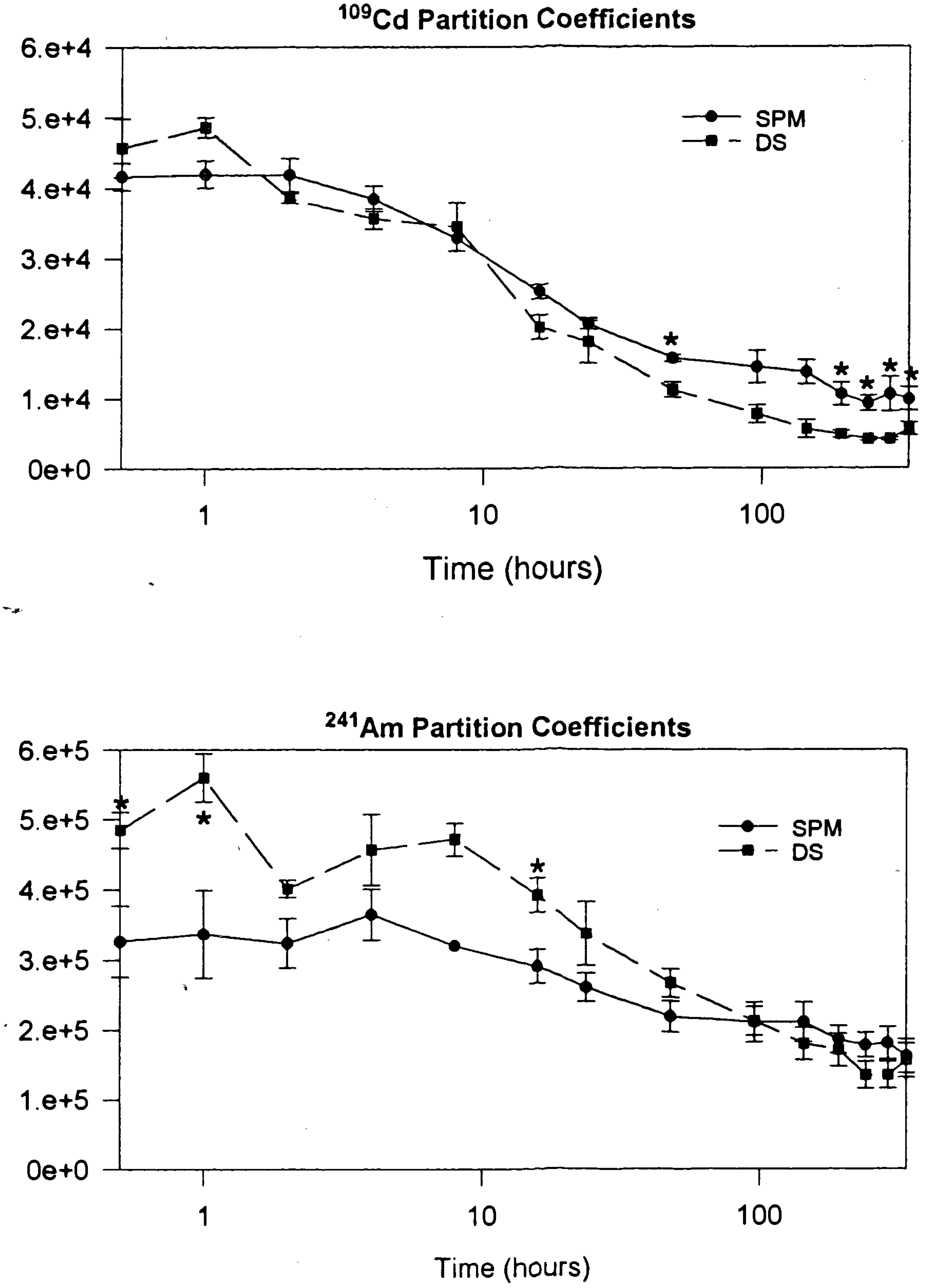


Figure 6.3 Radioisotope partition coefficients in SPM and DS



similar, but diverged over time, with SPM K_ds significantly greater than DS K_ds at hours 48, 144, 192, 240, and 288 (of a total duration of 336 hours). The partition coefficients of ^{241}Am started out significantly higher in DS than SPM (at hours .5, 1, and 16) and converged over time. The values crossed with the K_d of SPM being larger than DS after 96 hours. The activity of both isotopes associated with the walls of the aquaria and the millipore membrane and it's frame were assessed to assure the quality of these results. The activity of ^{109}Cd associated with aquaria was approximately 0.7% of the total ^{109}Cd desorbed into the water column; for ^{241}Am , this percentage was 11%. The difference between these two percentages again demonstrates stronger sorption characteristics of ^{241}Am than ^{109}Cd.

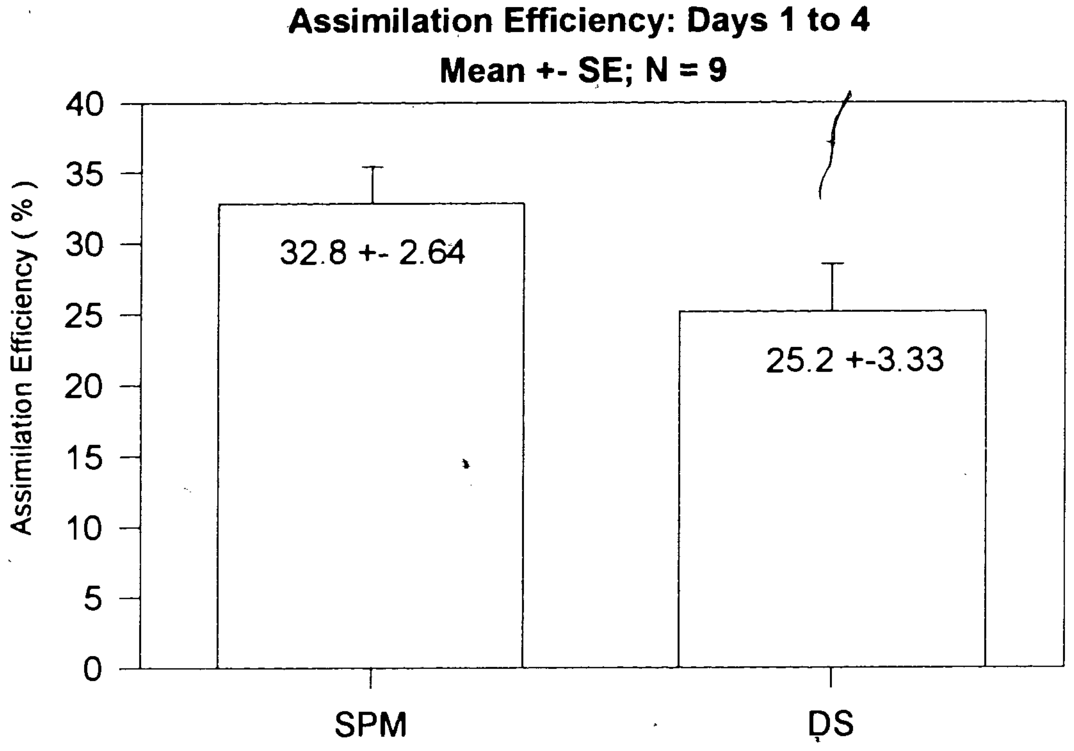
1.4 Assimilation Efficiency

The assimilation efficiencies of ^{109}Cd by *P. staminea* averaged over the first four days of exposure is 32.8 ± 2.6 % from SPM and 25.2 ± 3.3 % from DS (Figure 6.4 top). Averaged over eight days of exposure, ^{109}Cd assimilation by *P. staminea* is 33.3 ± 1.9 % from SPM and 18.9 ± 6.7 % from DS (Figure 6.4 bottom). All assimilation efficiencies were calculated using a food term corrected for both decay and desorption. Inclusion of the fourth sampling results in a significant drop in AE from DS due to significant desorption of ^{109}Cd from DS relative to SPM (Figure 6.2). In both cases, assimilation efficiency from SPM was found to be greater than from DS; however, the differences were not statistically significant at the 0.05 level (P=0.15, P=0.08, respectively).

1.5 Uptake

Uptake of ^{109}Cd from SPM and DS was measured in *P. staminea* and *M. balthica* (Figure 6.5). The organisms were exposed to ^{109}Cd in the water and in particulate form at environmentally realistic levels (Figure 6.6). Activities reported for *P. staminea* are for the tissue of depurated organisms, the activities reported for *M. balthica* are for whole depurated organisms. The proportion of activity associated with *M. balthica* tissue versus total activity was determined to be 0.72, or 72% of the total. With *M. balthica*, most ^{109}Cd uptake occurred over the first two days of both experiments with

Figure 6.4 Assimilation efficiency from SPM and DS



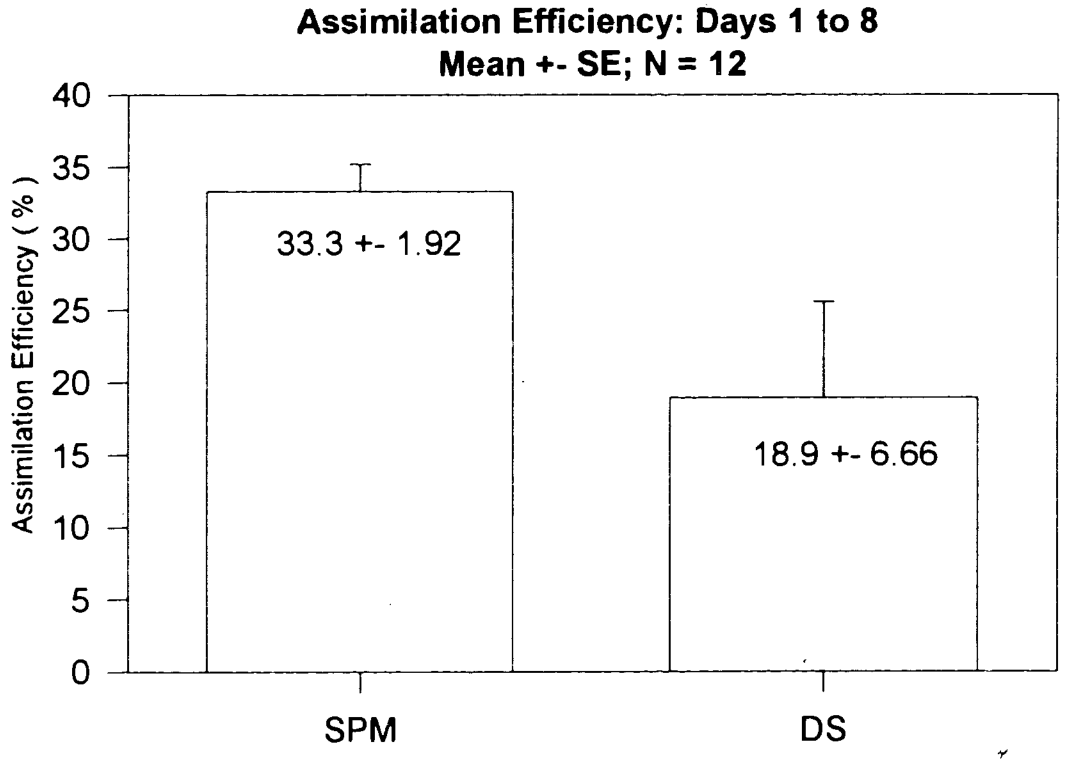
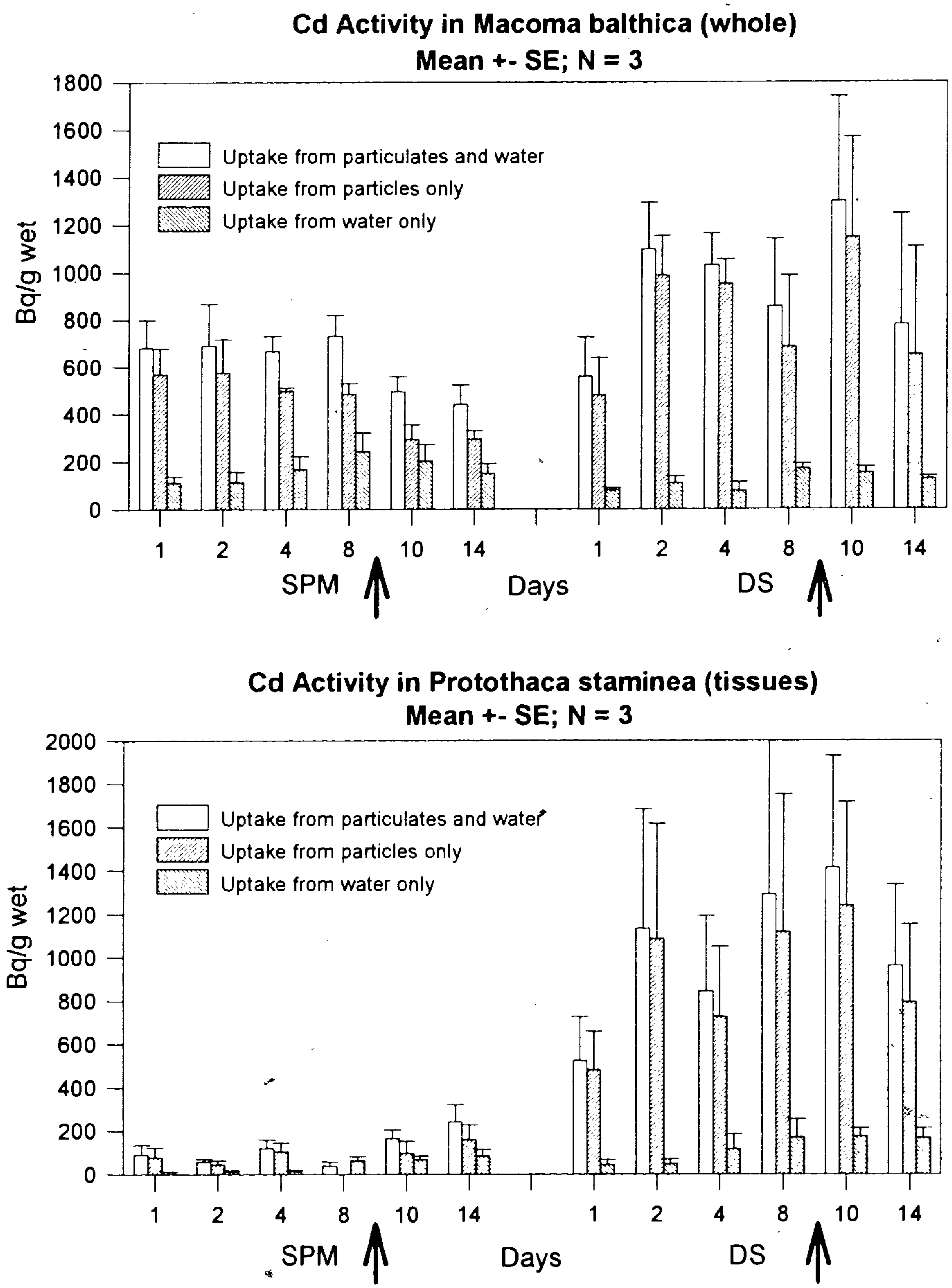
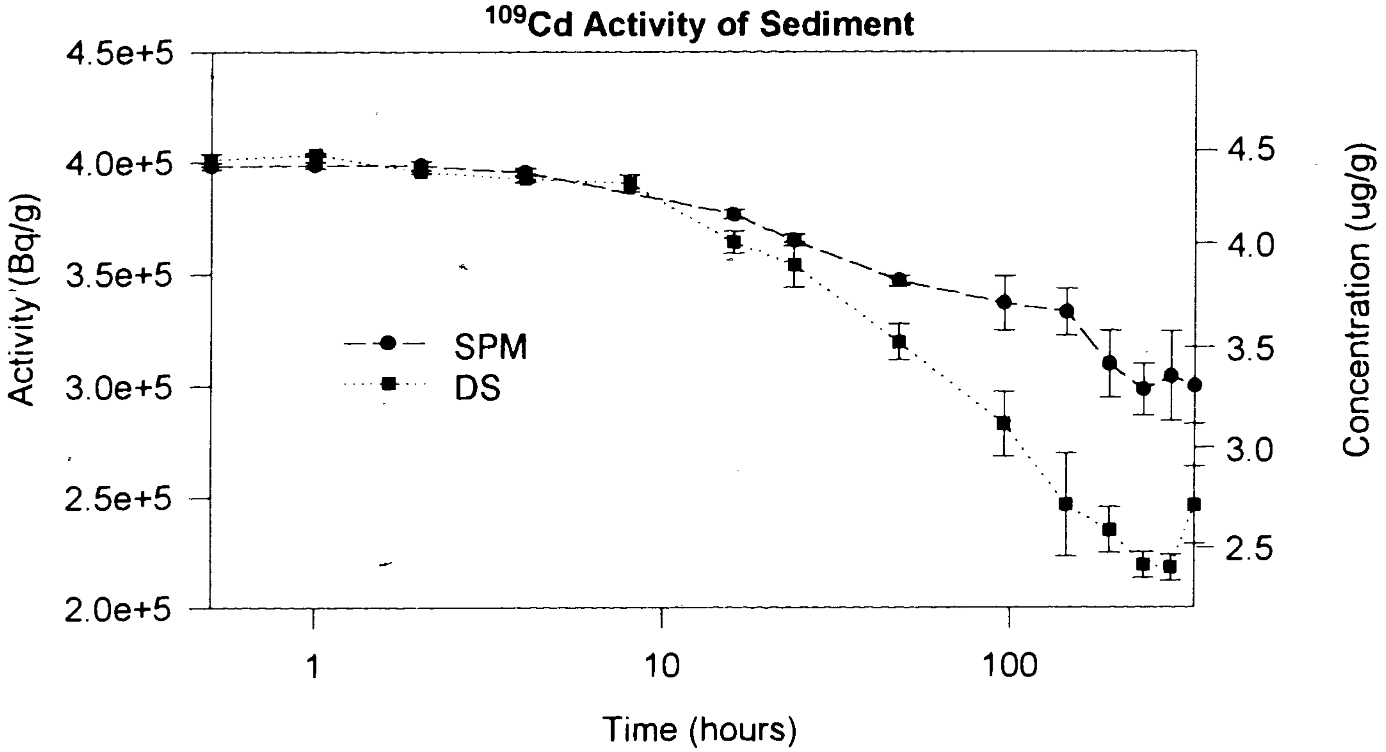


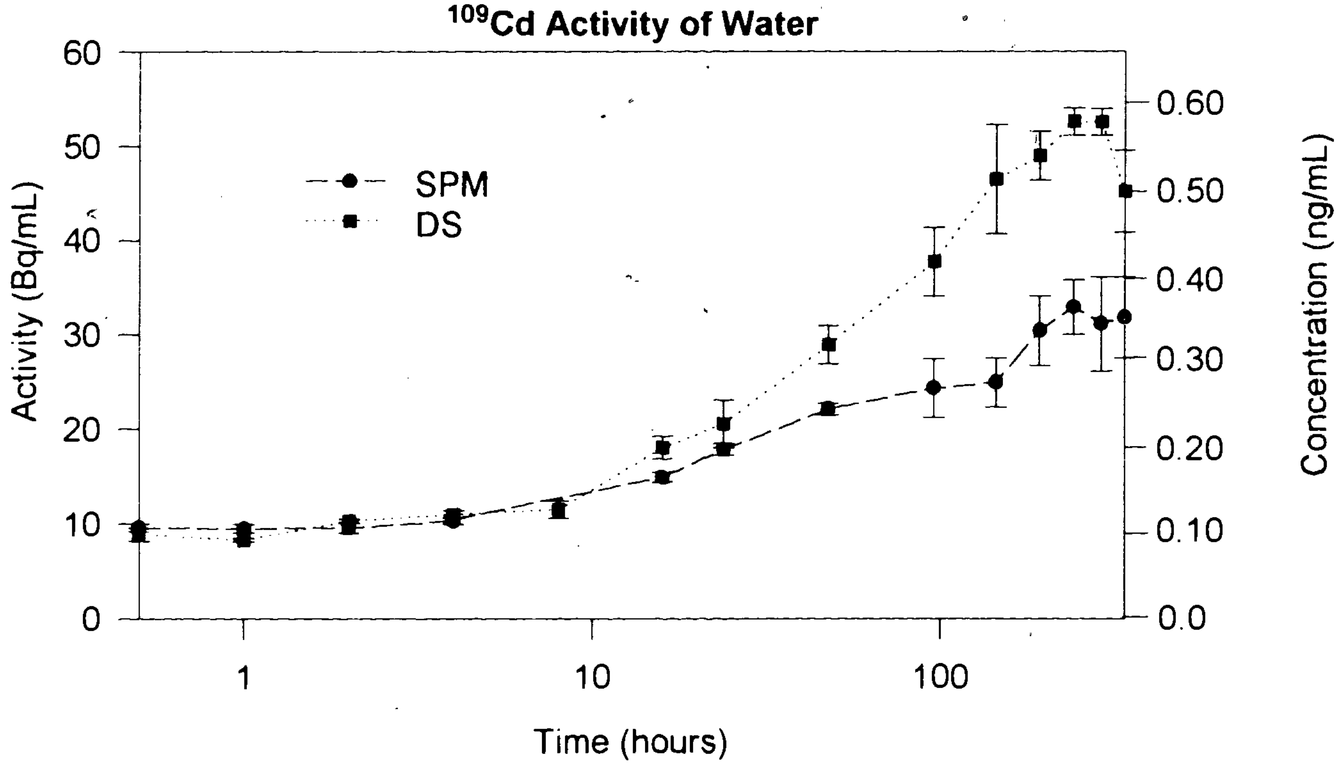
Figure 6.5 ^{109}Cd uptake from SPM and DS in *Macoma balthica* and *Protothaca staminea*



↑ Arrows indicate the beginning of depuration

Figure 6.6 ^{109}Cd activity in the sediment and water of exposure vessels





subsequent days showing either lower net uptake or net loss. Following the removal from the exposure vessel on day 8, ^{109}Cd levels in *M. balthica* decrease. This depuration is evident in both the particulate and water, and the water only exposures. In the DS exposure, most of the uptake by *P. staminea* occurred over the first two days, with consistently low uptake on subsequent days. Decreased ^{109}Cd levels are observed following depuration. During the SPM exposure, *P. staminea* showed a consistently low uptake and the expected depuration pattern was not observed. Rather, ^{109}Cd concentrations increased during depuration.

In the DS exposures, *M. balthica* took up 86.8 ± 4.0% (mean ± SE) of it's ^{109}Cd from the particulate phase, while *P. staminea* took up 90.6 ± 2.1% from the particulate phase. In the SPM exposures, *M. balthica* took up 78.9 ± 3.8% ^{109}Cd from the particulate phase, while *P. staminea* took up 80.8 ± 7.3 % from the particulate phase. Two way ANOVA of the arcsine transformed data indicates that the effect of sediment type is significant (N=48, F=6.44, P=0.015) while organism type and the interaction are not. Because the quantity of food consumed by these organisms was not measured, no comparisons based upon total uptake can be made.

2.0 DISCUSSION

An important area of scientific research involves the determination of the route of metal uptake in organisms (Timmermans, 1993). Two major pathways for uptake exist: 1) from the solute phase (dissolved metal), and 2) from the particulate phase (sediment and food particles). In most organisms, body metal concentrations will be the direct result of these two processes. Clear indications have been found that trace metals can be accumulated from food (i.e., Harvey and Luoma, 1985a; Dallinger and Kautzky, 1985; Timmermans, 1993, Thomann et al., 1995; Wang et al., 1995). To determine the relative importance of the two, methods to isolate the two components have been developed. Assimilation efficiencies use food and feces only to determine assimilation, while simple uptake experiments make use of membranes that allow the passage of dissolved metal forms. These techniques are applied in SPM and DS exposure experiments attempting to relate geochemical differences to differences in ^{109}Cd assimilation and/or uptake.

2.1 Sediment Geochemistry

The geochemical characteristics of the sediments used in the exposure experiments are reflective of the general observations of chapter 4. SPM is found to have higher concentrations of organic matter (LOI), iron oxides (reducible iron) and manganese oxides (easily reducible manganese) than DS. While LOI was not found to differ significantly between the two sediments, both reducible iron and easily reducible manganese were significantly greater in SPM than DS. The proportions of these three geochemical sediment features among the two sediments is similar. Specifically, the ratio of organic matter to iron oxides is 5.28 in SPM and 6.40 in DS; the ratio of organic matter to manganese oxides is 156 in SPM and 213 in DS; and the ratio of iron oxides to manganese oxides is 29.5 in SPM and 33.2 in DS. Thus the major difference between the two sediments appears to be related to absolute concentrations rather than proportional differences in constituents. However, since organic matter and oxides are of a heterogeneous nature, this does not preclude the partitioning differences noted in chapter 4. Geochemical differences in the two sediments will be considered in relation to both assimilation and uptake (sections 2.4 and 2.5, respectively).

2.2 Isotope Partitioning in DS and SPM

Differences in partitioning were noted between the two isotopes. ^{109}Cd was found to associate predominantly with the reducible and easily reducible phases of the sediments. No significant differences in ^{109}Cd partitioning was observed between the two sediments. The only other study of the partitioning of ^{109}Cd, although in soil rather than sediment, confirms the affinity of ^{109}Cd for the easily reducible phase (Riise et al., 1994). The lack of a partitioning difference between the two sediments suggests that the excess of binding sites allowed ^{109}Cd to associate with the sediment in proportions resulting from the chemical properties of ^{109}Cd, not the sediments. ^{241}Am was found to associate predominantly with the reducible phase, with much less partitioning to the easily reducible phase than observed with ^{109}Cd. Differences were observed in the way ^{241}Am partitioned in the two sediments. More ^{241}Am partitioned to the easily reducible phase of DS than SPM, with the opposite observed for the partitioning to the reducible and organic phases. This difference is difficult to understand given the excess of sediment binding phases, but could be due to differences in the nature of the oxides (which can vary from amorphous to crystalline) or to differences in the heterogeneous organic matter.

2.3 Isotope Desorption and Mass Balance

In static exposure systems, following the addition of spiked material, it is expected that redistribution will occur, specifically, desorption to the water column is expected. In this experiment, it is shown that the desorption of both ^{109}Cd and ^{241}Am from sediments occurs over time. A greater amount of ^{109}Cd desorbs from DS than from SPM, while there is no significant difference observed for ^{241}Am. This is likely the result of the geochemical differences in the two sediments. Specifically, the SPM has a higher concentration of metal binding phases and is therefore expected to bind the isotope more effectively. The partition coefficients of both metals decreased over the course of the experiments reflecting this desorption. Partition coefficients for ^{109}Cd were in the $1 - 5 \times 10^4$ range, while they were in the $2 - 5 \times 10^5$ range for ^{241}Am. Decho and Luoma (1994) found a K_d of 1.8×10^4 when iron oxides coated with fulvic acids were spiked with similar levels of ^{109}Cd. Vangenechten et al. (1983) found K_ds for ^{241}Am ranging from $1.5 - 1.8 \times 10^5$ in marine sediments. Importantly, sorption of isotope to aquaria and membranes was negligible in comparison to the activity of isotope in dissolved form (<0.45μm). These significant desorption characteristics have bearing upon the results of the assimilation and uptake experiments and will be discussed in sections 2.4 and 2.5, respectively.

2.4 Assimilation Efficiency

The importance of sediment geochemistry in influencing metal assimilation has been assessed primarily by Luoma and colleagues (Luoma and Jenne, 1976, 1977; Harvey and Luoma, 1985a,b; Wang et al., 1995), and numerous researchers have shown that geochemistry influences metal uptake (Diks and Allen, 1983; Tessier et al., 1984; Bendell-Young and Harvey, 1991). The sediments used in the exposure experiments differ significantly in their concentrations of easily reducible manganese and reducible iron, with both being significantly higher in SPM than in DS. The exposure conditions (2.5-4.5 μg/g and 0.2-0.6 ng/mL ^{109}Cd at 12°C and 14 ppt salinity) were environmentally realistic. Although the differences in assimilation efficiency were greater in SPM than in DS, the differences were not significant at the $P=0.05$ level.

Assimilation of particle bound metals is believed to involve their conversion from particulate to dissolved form in the gut, followed by competition with gut components and facilitated diffusion across the interstitial membrane (Luoma, 1983). In bivalves, glandular digestion can also occur (Widdows et al., 1979; Decho and Luoma, 1991; Wang et al., 1995). Most observations have suggested that easily reducible metal is most available to organisms since it is most easily dissolved. For example, metals associated with manganese oxides (easily reducible manganese) have been shown to be 100 times more available to *Macoma balthica* than from other components (iron oxides [reducible iron] and organic matter; Luoma and Jenne, 1977). Diks and Allen (1983) suggest that the high correlation between metal uptake in tubificid worms and metal present in the easily reducible phase (associated with Mn oxides) suggests that the redox potential and pH in the gut of these worms are such that Mn oxide coatings are dissolved. In heterogeneous sediments, the presence of iron oxides as a dominant component of sediment has been shown to result in undetectable Cd uptake from ingestion (Luoma and Jenne, 1977; Harvey and Luoma, 1985b). While particulate bound Cd has been shown to be available to *M. balthica* from estuarine sediments, Cd bound to iron oxides (geothite) has been shown to be essentially unavailable to these organisms (Harvey and Luoma, 1985b). However, Luoma and Jenne (1976) found that Cd from uncoated iron oxides was more available to *M. balthica* than Cd associated with organic detritus. Similarly, Decho and Luoma (1994) found that bivalves absorbed Cd bound to uncoated iron oxide (geothite) or silica particles. The presence of organic coatings on particles reduced Cd bioavailability relative to uncoated particles. Harvey and Luoma (1985b) suggest that the presence of bacteria in sediment can stimulate enzyme secretion and that enzymes are capable of competing with iron oxides in the digestive tract of *M. balthica*. Since bacteria are generally associated with organic material (and indeed contribute to organic material), organic matter levels in sediments could interact with digestive physiology through it's bacterial complement. Overall, it appears that the concentrations of iron oxides and organic matter in the sediment act as trace metals sinks, rendering them less available (i.e., Tessier et al., 1993). Thus, the interplay of geochemical components is important to metal availability. The assimilation of metal will therefore be the result of a combination of the digestibility of sediment components, gut physiology; and competition from undigested components.

The geochemical differences between SPM and DS used in these experiments were consistent with sediment observations made throughout the study, especially during conditions of lower flow. Specifically, higher concentrations of both easily reducible manganese and reducible iron were found in SPM than in DS. Keeping these differences in mind, the efficiency with which ^{109}Cd was assimilated by *Protothaca staminea* from SPM was somewhat greater than the efficiency with which it was assimilated from DS. This difference was not statistically significant at P=0.05, although over the course of 8 days the probability of a type I error was only 0.08. It has been suggested that *Mytilus edulis* can alter it's gut passage time (GPT) in response to food quality (Bayne et al., 1987). Such a response in *P. staminea* to the higher organic content of SPM could result in higher assimilation efficiency. The lack of a strong significant effect of geochemistry could be due to the geochemical similarity of the two sediments discussed in section 2.1 and the similar partitioning observed in the two sediments (section 2.2). In addition, it must be recalled that organisms were sacrificed at each sampling and each assimilation efficiency is calculated with a different set of organisms. While the sediment did differ substantially in the contents of binding phases, they did not differ in the relative proportions of the binding phases, and it could well be these proportions that determine availability. While the partitioning of cadmium in the two sediments was similar when spiked with cadmium, this was not observed with metals in Fraser River Estuary sediments (Chapter 4, section 1.5).

The assimilation efficiency (AE) of ^{109}Cd from SPM (33%) and DS (19 to 25%) compares favourably to the AEs found by other experimenters. Decho and Luoma (1994) found AEs between 23 and 42% in *M. balthica* depending in the geochemical nature of formulated sediments and the concentrations of metals used (from 1/10 to 8 x those used in the present experiment). From uncoated iron oxide particles, they found an AE of 34 ± 13% in *M. balthica*. Wang et al. (1995) found AEs between 30 and 45% in *Mytilus edulis* under differing food (algae *Thalassiosira pseudonana*) rations. They note that AEs decrease with increasing ingestion rate over the range studied. They also found that if ^{109}Cd was retained for longer than 17 h in the digestive tract, it was assimilated. Thus, the 24 h depuration period used in the present experiments is appropriate. Wang and Fisher (1996) found an AE of 21% in *M. edulis* fed glass beads to which ^{109}Cd was sorbed, supporting the capacity of the bivalve gut to remove sorbed metals. From different algae species they note AEs from 11.3 to 28.3%. The differences between species suggest that different species have differing abilities to sequester metals, making them more or less available to consumers. Once assimilated, other research suggests that cadmium is relatively slowly excreted, with biological half times of 3-7 months in mussels (Borchardt, 1983; Viarengo et al., 1985).

Assimilation efficiencies in the range of 25 to 33% suggest that all metal input into the aquatic environment is important since a substantial portion to which an organism is exposed (in food) can be assimilated. As shown in Chapter 4, the most nutritional food also contains the highest concentration of contaminants. In the case of natural sediments, it appears that this nutritious, contaminated food is also the material from which organisms can most easily assimilate metal. In addition, the geochemical analyses carried out suggest that the concentration of metals in SPM is much greater than in DS, especially during low river flow. It therefore seems probable that the greater concentrations and the greater or equal AEs combine to make SPM a more significant source of contaminants to organisms. In this regard, it is important to consider when, where, and which organisms will be exposed in order to identify periods of potentially high metal uptake.

Assumptions

- Assimilation efficiencies determined by the twin tracer method are an effective and simple means to directly determine the bioavailability of a metal from food to a test organism. Importantly, the technique does not suffer from some of the drawbacks of simple uptake experiments discussed in the next section. However, the term "assimilation efficiency" is somewhat of a misnomer and is therefore operationally defined as the quantity measured by the twin tracer method of Fisher and Reinfelder (1991). Assimilation efficiency via the twin tracer method is more accurately a measure of corrected retention efficiency. Clarity on the definition of assimilation is important. Assimilated elements are those that are taken up by organisms and used in a structural or functional sense; that is, they become part of an organism's structural or metabolic machinery. Absorbtion, on the other hand, implies that an element is transported across the gut (or other surface) into the internal environment of an organism. Generally, assimilated material is a subset of absorbed material. Lastly, retention is simply any material that is taken up by an organism but doesn't make it back out of the organism. Processes are not considered in retention, and experiments are generally undertaken at time intervals that are synchronous with known gut passage times of the test organism. Generally, absorbtion is a subset of retention. Thus, retention relative to an inert tracer is measured in the twin tracer method. This is essentially corrected retention efficiency with the assumption that differences between the two isotopes represent metal that has been assimilated.

Several important assumptions of the twin tracer method must be considered in the context of the present experiment. The twin tracer method assumes that the element under investigation passes through the digestive tract at a rate similar to that of the inert tracer and that rates of loss from the feces into the dissolved phase are comparable (Wang and Fisher, 1996). Wang et al. (1995) have demonstrated that this is a concern for the ^{109}Cd and ^{241}Am pair, especially at higher feeding rates, but is less significant than with other isotopes. The importance of this observation decreases with the duration of the experiments, and is likely to be less important in longer experiments of greater than 1 day. Wang and Fisher (1996) found that the gut passage time (GPT) of ^{241}Am in *Mytilus edulis* was <17h, while any ^{109}Cd that had not passed through the gut by this time was assimilated. In the present experiments, organisms were allowed to depurate for 24 hours before collection and analysis of the feces. This interval seems appropriate given the findings of Wang and Fisher. Reinfelder and

Fisher (1991) found that GPT was not affected by cell density in algal suspensions from 0.25 to 2.02 mgdw/L and Wang et al. (1996) found that food concentration had little influence on AEs for Cd within the range of 16 to 800 µgC/L. These observations suggest that the organism, rather than food concentration control GPT. Another assumption is that loss of isotope from the feces (to the depuration water) is similar for the two isotopes. Given the low activity of feces, it is unlikely that desorption of either isotope is significant, although desorption of ^{109}Cd would be greater than ^{241}Am.

In addition to the assumptions of the twin tracer method, there is an important assumption of the experimental design in the present study. This is that *Protothaca staminea* is exposed to representative particles in both experiments. Since *P. staminea* is a filter feeder, the possibility exists that it was disproportionately exposed to smaller, suspendable particles in the DS experiment. However, since this occurrence would favour enhanced exposure to ^{109}Cd from DS, any bias introduced would not alter the findings of this experiment although it may have reduced the magnitude of the differences observed between AE from SPM and DS.

Implications of isotope desorption

The effects of the desorption of the isotope from the sediment into the water were accounted for in the calculation of assimilation efficiency. In addition, the contribution of uptake from desorbed ^{109}Cd to feces was subtracted. It is interesting to note that consideration of the desorption of isotope from the food results in the calculation of lower AE than if desorption were not considered. Since the desorption of ^{109}Cd was greater from DS than SPM, calculation of AE without desorption would yield AEs for SPM and DS that are very close. AEs calculated without desorption over eight days of exposure are 35.4 ● 1.9 % from SPM and 32.7 ● 2.2 % from DS. This observation emphasizes the importance of considering desorption when conducting experiments over time periods where desorption is significant.

In the depuration vessel, isotope could desorb from feces into the depuration water. This effect could reduce the feces Cd/Am ratio (since Cd was shown to desorb more readily than Am), thereby decreasing the calculated AE. While this effect is likely to decrease the AE somewhat, it is unlikely to make a significant difference. The only comparison available is the desorption from sediment in the exposure vessels and it's effect on partitioning coefficients (Figure 6.2). In this case, after 24 hours (the maximum period that feces could sit in the depuration vessels), 15% of the isotope had desorbed. However, three factors contribute to make this an overestimate of the isotope that would desorb from the feces. Firstly, the sediment added was concentrated (440 kBq/g), while the feces generally had an activity of 10 to 30 kBq/g. Second, sediment was added to a very turbulent system designed to keep the sediment in suspension, while the defecation occurred in the quiescent depuration chambers. Third, the feces, having passed through the organisms is likely to have reduced amounts of readily desorbable isotope. The combination of these observations suggests that desorption from feces was likely a minor factor influencing AEs.

Applicability of assimilation efficiency to heterogeneous substrates

The use of the assimilation efficiency methods appears to be of substantial usefulness in the effort to understand the relationship between assimilation and geochemistry. An improved understanding of assimilation from homogeneous substrates would be useful. In addition, this study indicates that in heterogeneous substrates, consideration must be given to the relative proportion of each substrate, which may be more important than absolute quantities in governing the assimilation of isotopes. Manipulation of the relative proportions of these substrates in environmentally realistic fashion and subsequent assimilation experiments would be informative.

2.5 Uptake

The uptake of ^{109}Cd by the test organisms *P. staminea* and *M. balthica* was assessed. These experiments were designed as assimilation experiments and were therefore of short duration, and since the quantity of sediment consumed by the organisms is not known, comparisons of total levels in the organisms cannot be made. However, examination of the uptake data provides some useful information. Specifically, these experiments demonstrate a very low uptake from sediment on a concentration for concentration basis, yet show that the particulate phase is the more important route of ^{109}Cd uptake by both organisms under the conditions and duration of this exposure. This is due to the very high concentrations in the sediment relative to water. The concentration of isotope in both the sediment (mean concentration of approximately 350 kBq/g or 3.9 µg/g) and water (mean concentration of approximately 30 Bq/mL or 0.33 ng/mL) and the exposure conditions of 14 ppt salinity and 12°C were environmentally realistic.

The observations demonstrate the high variability involved in working with these organisms, as noted by Harvey and Luoma (1985b). This variability arises because the organisms were field collected and were potentially of different ages. In addition, the *P. staminea* used to calculate uptake at each interval were different groups since organisms were sacrificed at each sampling. The bulk of the uptake occurred over the first two days and decreased subsequently (Figure 6.5). Similar observations were made by Harvey and Luoma (1985b) for ^{109}Cd uptake by *M. balthica* from bacteria *Pseudomonas atlantica* and by Absil et al (1994), who note that most ^{64}Cu uptake occurred in the first 5-10h of exposure in *M. balthica*. Both test organisms took up more isotope from the particulate phase than from the water and a significantly higher proportion of uptake from the particulate phase occurred in DS than in SPM. *M. balthica* took up 87% of its ^{109}Cd from particulates in the DS exposures and 79% in the SPM exposures. *P. staminea* took up 91% of it's ^{109}Cd from the particulate phase in the DS exposures and 81% in the SPM exposures. This suggests that particulates represent a more important uptake route in these organisms. In addition, more ^{109}Cd desorbed from DS than from SPM and appears to be related to bioavailability of ^{109}Cd from the particulate phase. In *M. balthica*, more ^{109}Cd was taken up in the DS exposure than in the SPM exposure. However, water uptake differs in the opposite direction. These two results are compatible if one considers that the higher desorption of ^{109}Cd from DS than SPM suggests that it is more weakly associated with DS than SPM. If this is the case, proportionally more particulate uptake is expected from DS than SPM, as is in fact noted.

The proportional values determined here are similar to the 94% particulate uptake estimates by Thomann et al. (1995). They suggest that this high proportion could be due to the induction of metallothionein (i.e., Roesijadi, 1992), resulting in high assimilation and low depuration rates. Indeed, this is supported by the observed high biological half time (3-7 months) of Cd (Borchardt, 1983; Viarengo, 1985). However, Harvey and Luoma (1985b) suggest that this ratio would decrease over the longer term. In their experiments, uptake from particulates contributed 67% of the total after 2 days, 50% of the total after 8 days, but only 39% of the total after 14 days. They suggest that this is due to isotope depletion in the bacteria they were using as particulate food for *M. balthica*. However, in their experiment, depletion of ^{109}Cd was much greater than in the present experiments. They note that only 6.7% of the original ^{109}Cd activity was still associated with bacteria after 4 days. In comparison, 77% of the ^{109}Cd added to SPM and 65% of the ^{109}Cd added to DS was still associated with the particulates after 4 days in the present experiments.

Experimental Considerations

Assessing uptake in such an experiment suffers from several major drawbacks. The first is the degree of similarity between experimental compartments when all start from the same point. Stochastic processes and subsequent inertia can result in substantial differences in the interaction between metal and organism behaviour. The second drawback is that the quantity of food consumed by the organisms is unknown. Many factors can influence the biological response to different foods and differences in uptake are due to the interaction between the nature of food (geochemistry) and biological response. Thus without knowing the biological response, differences in uptake cannot be definitively attributed to differences in food alone. The third drawback is that, when using field-collected organisms, the inter-individual differences can be high. The assimilation efficiency method is less affected by these problems, because only two simple measurements are required; ratio in the food and ratio in the feces. These are not influenced by as many biological factors.

In comparing uptake from the water phase with uptake from particulates, it is important to note that control organisms did not have food. The absence of food could alter the filtering activity of the organisms. A difference in filtering activity will affect how much dissolved metal an organism is exposed to. If food were added to the exposure vessel, dissolved metal would sorb to the food and uptake via the particulate route would occur. Therefore, there is no perfect control for this experiment, and the relative uptake of ^{109}Cd obtained in this experiment must be explained only with a clear description of the experimental conditions. It has been suggested that starved animals may accumulate metals more rapidly than feeding animals (Luoma and Jenne, 1976; Klump, 1980). They suggest that food can enhance efflux by providing metal binding phases in the gut. The absence or shortage of food has been observed to cause strongly reduced ventilation rates (Riisgard and Randlov, 1981; Hummel, 1985) and therefore less uptake of dissolved metals. It has been suggested that starved bivalves have reduced filtration rates and consequently accumulate fewer metals (Borchardt, 1985; Riisgard et al., 1987). However, the presence of food has also resulted in reduced filtration rates in *M. balthica* and *Cerastoderma edule* (Absil et al., 1996). In addition, the presence of food will influence the metabolic condition (Bayne et al., 1988) so accumulation as well as elimination rates of metals can be increased (Borchardt, 1983). Therefore, it is unclear whether the controls represent an overestimation or underestimation of ^{109}Cd uptake via the water route in the treatment organisms.

Behavioral considerations

In any consideration of uptake, the behavioral characteristics of a test organism must be taken into account. In the present case, the feeding characteristics of the two clams differ substantially. *M. balthica* is a facultative filter feeder, that can "vacuum" bottom sediments with it's long siphon with some selectivity (Absil et al., 1996). *M. balthica* is also able to filter food from the overlying water column while the inhalant siphon is just at the sediment surface (Brafield and Newell, 1961; Hummel. 1985). While deposit feeding the clam extends it's inhalant siphon over the sediment surface (Zwarts and Wanink 1989) which may require reduction in the clam's burial depth. *P. staminea* is an obligate filter feeder that relies exclusively upon inhalant water currents to take up food via it's short siphons (Crecelius et al., 1982; George and George, 1979). The objective of filter or deposit feeding is to maximize ingestion of adsorbed bacteria and surface organic coatings and therefore, small particles are preferentially ingested (Luoma and Davis, 1983). Both can sort food according to size and specific gravity via a complex muco-ciliary mechanism associated with the gill and palps (Jorgensen, 1990). Acceptable food is swept to the oral groove and into the stomach; unacceptable food is rejected as pseudofeces (Jorgensen, 1990). Thus, the mechanism of feeding and the degree of selectivity can have a substantial influence upon metal uptake. During the SPM exposure experiment, it is apparent that *P. staminea* did not take up much metal relative to *M. balthica* or to the DS exposures. A probable reason for this is that in the SPM exposure, the aquarium water was very murky, with most of the SPM remaining suspended. This would present *P. staminea* with a situation in which it's sorting mechanism would simply be overwhelmed. In the DS experiments the water was not as murky (since the larger sediment particles settled to the bottom) and therefore *P. staminea* was able to filter in an uninterrupted manner. Since *M. balthica* can "vacuum" the bottom and need not rely upon inhalant currents, it was able to maintain consistent uptake in both experiments. This mechanism would also explain why ^{109}Cd activities in *P. staminea* increased upon depuration in the SPM exposure. If the organisms were able to clear the fouling SPM to the depuration chamber, they could then resume normal uptake.

Absil et al. (1996) contrasted the copper uptake from bed sediments in *M. balthica* (a facultative filter feeder [i.e., it can deposit feed]) and *Cerastoderma edule* (an obligate filter feeder). They found that *M. balthica* accumulated copper from the sediment whereas *C. edule* did not. As a result, only *M. balthica* was influenced by sediment geochemistry. Similarly, Crecelius et al. (1982) compares copper uptake in *P. staminea* (an obligate filter feeder) and *M. inquinata* (a deposit feeder). In a sediment/water system, they found that copper was unavailable to *P. staminea* but available to *M. inquinata*. Their exposure design selectively exposed *M. balthica* since only *M. balthica* is expected to be able to access bottom sediment. *P. staminea* had gill copper levels 170 times higher than controls. In the present investigation, similar behavioural differences could occur in the exposure systems.

Implications of isotope desorption

Luoma and Jenne (1977) found that uptake of isotopes of Ag, Co and Zn from water and particulates in *M. balthica* was a strong function of sediment-solute distribution. They concluded that the distribution ratios and therefore metal uptake were controlled by binding intensity. The process that controlled desorption of the nuclides from sediment to water was similar to the process that controlled metal uptake during digestion. If this is demonstrated to be consistently the case, Jenne et al. (1986) suggest that bioavailability from both ingestion and solution could be estimated from determination of free ion concentrations in solution at equilibrium with sediments, since the processes that control metal desorption from sediment are similar to the processes that control metal uptake during digestion. In the present situation, and in the environment, where binding sites are in excess of metals, this arises due to the heterogeneity of binding sites. Specifically, strong binding sites are saturated first, followed by progressively weaker sites. A greater proportion of strong binding sites (i.e., SPM vs. DS) will result in lower desorption and reduced uptake. Based upon the results of ^{109}Cd uptake (but not assimilation efficiency) this appears to be valid, the extent of desorption appears to be related to uptake from particles suggesting the possibility that desorption is an effective measure of the availability of particulate associated metals in experiments where particle-associated metal is oversaturated with respect to the water.

2.6 Relative Importance of SPM and DS

The results of this chapter provide some important information regarding the relative importance of SPM and DS as vectors for the transfer of metals to aquatic organisms. This chapter has shown that assimilation from the two sediments is similar when the geochemistry differs only in scale and the partitioning is the same. The observations of chapter 4 suggest that this is not the case with most sediment-associated metals in the Fraser River. Specifically, metals partition to relatively more easily dissociable phases in SPM than in DS. In addition, concentrations of metals associated with SPM are often an order of magnitude greater than DS. Therefore, a major finding of this study is that organisms could take up more metal when exposed to equivalent quantities of SPM than DS. This observation must be linked to the relative importance of exposure to each vector on an organism by organism basis. The accumulation of metals in natural systems will depend mainly upon the natural behaviour of a particular organism (i.e. section 2.5 and Absil et al., 1996), and the relative quantity and bioavailability of metals in phases important in the exposure of the organism.

For the facultative filter feeder, *M. balthica*, the differences between the two sediments are especially important, since the organism can consume either. Bubnova (1972) and Olafsson (1986) hypothesize that *M. balthica* suspension feeds when suspended food particles are abundant and deposit feeds when suspended food supply decreases. Thus, the organisms can effectively "decide"whether to filter feed depending upon the quality of the food. It might also be hypothesized that the organism can respond in a similar manner to contamination. The problem is that the two are directly related since SPM provides a more nutritious and more contaminated food source. In addition, the lower burial depth that filter feeding allows *M. balthica* makes it less susceptible to predation (Reading and McGorty, 1978; Blundon and Kennedy, 1982; de Vlas, 1979, 1985; Hines, 1990). Research has indicated that the greater part of the food of *M. balthica* is suspended matter (Hummel, 1985; Thompson and Nichols, 1988; Beukema and Cadee, 1991). Given that both test organisms consume suspended particulates and one has a choice, it is possible that *M. balthica* could avoid metal uptake when concentrations are high.

3.0 REFERENCES

Absil, M.C.P., M. Berntssen and L.J.A. Gerringa. 1996. The influence of sediment, food and organic ligands on the uptake of copper by sediment-dwelling bivalves. Aquat. Toxicol. 34: 13-29.

Bayne, B.L., J.S. Hawkins and E. Navarro. 1988. Feeding and digestion in suspension feeding bivalve molluscs: the relevance of physiological compensations. Am. Zool 28: 147-159.

Bayne, B.L., J.S. Hawkins and E. Navarro. 1987. Feeding and digestion by the mussel *Mytilus edulis* L. (Bivalvia: Mollusca) in mixtures of silt and algal cells at low concentration. J. Exp. Mar. Biol. Ecol. 111: 1-22.

Bendell-Young, L.I. and H.H. Harvey. 1991. Metal concentrations in chironomids in relation to geochemical characteristics of surficial sediments. Arch. Environ. Contam. Toxicol. 21: 202-211.

Beukema, J.J. and G.C. Cadee. 1991. Growth rates of the bivalve *Macoma balthica* in the Wadden Sea during a period of eutrophication: relationships with concentrations of pelagic diatoms and flagellates. Mar. Ecol. Prog. Ser. 68: 249-256.

Blundon, J.A. and V.S. Kennedy. 1982. Refuges for infaunal bivalves from the blue cran, *Callinectes sapidus* (Rathbun), predation in Chesapeake Bay. J. Exp. Mar. Biol. Ecol. 60: 17-34.

Borchardt, T.. 1985. Relationship between carbon and cadmium uptake in *Mytilus edulis*. Mar. Biol. 85: 233-244.

Borchardt, T.. 1983. Influence of food quantity on the kinetics of cadmium uptake and loss via food and seawater in *Mytilus edulis*. Mar. Biol. 76: 67-76.

Brafield, A.E. and G.E. Newell. 1961. The behaviour of *Macoma balthica* (L.). J. Mar. Biol. Assoc. UK. 41: 81-87.

Bubnova, N.P.. 1972. The nutrtion of the detritus feeding mollusks *Macoma balthica* (L.) and *Portlandia arctica* (Gray) and their influence on bottom sediments. Oceanology 12: 899-905.

Crecelius, E.A., J.T. Hardy, C.I. Bobson. R.L. Schmidt, C.W. Apts, J.M. Gurtisen and S.P. Joyce. 1982. Copper bioavailability to marine bivalves and shrimp. Relationship to cupric ion activity. Mar, Environ. Res. 6: 13-26.

Dallinger, R. and H. Kautzky. 1985. The importance of contaminated food for the uptake of heavy metals by rainbow trout (*Salmo gairdneri*): a field study. Oecologia 67: 82-89.

Decho, A.W. and S.N. Luoma. 1994. Humic and fulvic acids: sink or source in the availability of metals to the marine bivalves *Macoma balthica* and *Potamocorbula amurensis*? Mar. Ecol. Prog. Ser. 108: 133-145.

Decho, A.W. and S.N. Luoma. 1991. Time-courses in the retention of food material in the bivalves *Potamocorbula amurensis* and *Macoma balthica*: significance to the absorption of carbon and chromium. Mar. Ecol. Prog. Ser. 78: 303-314.

Diks, D. and H.E. Allen. 1983. Correlation of copper distribution in a freshwater-sediment system to bioavailability. Bull. Environ. Contam. Toxicol. 30: 37-43.

George, J.D. and J.J. George. 1979. Marine life: an illustrated encyclopedia of invertebrates in the sea. John Wiley and Sons, New York.

Harvey, R.W. and S.N. Luoma. 1985a. Separation of solute and particulate vectors of heavy metal uptake in controlled suspension feeding experiments with *Macoma balthica*. Hydrobiologia 121: 97-102.

Harvey, R.W. and S.N. Luoma. 1985b. Effect of adherent bacteria and bacterial extracellular polymers upon assimilation by *Macoma balthica* of sediment bound Cd, Zn, and Ag. Mar. Ecol. Prog. Ser. 22: 281-289.

Hines, A.H., M.H. Posey and P.J. Haddon. 1989. Effects of adult suspension- and deposit- feeding bivalves on recruitment of estuarine infauna. Veliger 32: 109-119.

Hummel, H.. 1985. Food intake of *Macoma balthica* (Mollusca) in relation to seasonal changes in it's potential food on a tidal mudflat in the Dutch Wadden Sea. Neth. J. Sea Res. 19: 52-76.

Jenne, E.A., D.M. DiToro, H.E. Allen and C.S. Zarba. 1986. An activity-based model for developing sediment criteria for metals: Part 1. A new approach. In: Proceedings of the international conference on chemicals in the environment. J.N. Lester, R. Perry and R.M. Sterritt (Eds.). Salper, London. pp. 560-568.

Jorgensen, C.B.. 1990. Bivalve filter feeding: hydrodynamics, bioenergetics, physiology and ecology. Olsen and Olsen, Fredensborg, Denmark.

Klump, D.W.. 1980. Accumulation of arsenic from water and food by *Littorina littoralis* and *Nucella lapilus*. Mar. Biol. 58: 265-274.

Luoma, S.N.. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci. Tot. Environ. 28: 1-22.

Luoma, S.N.. 1982. Bioavailability of sediment -bound trace metals. U.S. Geological Survey Circular 969: 32-56.

Luoma, S.N. and J.A. Davis. 1983. Requirements for modelling trace metal partitioning in oxidized estuarine sedimentsemploying chemical extractants. Sci. Tot. Environ. 17: 165-196.

Luoma, S.N. and E.A. Jenne. 1977. The availability of sediment-bound cobalt, silver, and zinc to a deposit feeding clam. In: Biological implications of metals in the environment. R.E. Wildung and H. Drucker, (Eds.). NTIS CONF-750920, Springfield. pp. 213-230.

Luoma, S.N. and E.A. Jenne. 1976. Factors affecting the availability of sediment-bound cadmium to the estuarine deposit feeding clam, *Macoma balthica*. In: Radioecology and energy resources. E. Cushing (Ed.). Dowden, Hutchinson and Ross Inc., Stroudsberg: 283-291.

Olafsson, E.B.. 1986. Density dependence in suspension feeding and deposit feeding populations of the bivalve *Macoma balthica*: a field experiment. J. Anim. Ecol. 55: 517-526.

Reading, C.J. and S. McGorty. 1978. Seasonal variation in the burying depth of *Macoma balthica* (L.) and it's accessibility to wading birds. Eastuar. Coast. Shelf Sci. 6: 135-144.

Reinfelder, J.R. and N.S. Fisher. 1991. The assimilation of elements ingested by marine copepods. Science: 251: 794-796.

Riise, G., B. Salbu, B.R. Singh and E. Steinnes. 1994. Distribution of ^{109}Cd among different soil fractions studied by a sequential extraction technique. Wat. Air. Soil. Pollut. 73: 285-295.

Riisgard, H.U. and A. Randlov. 1981. Energy budgets, growth and filtration rates in *Mytilus edulis* at different algal concentrations. Mar. Biol. 61: 227-234.

Riisgaard, H.U., E. Bjornestad and F. Mohlenberg. 1987. Accumulation of cadmium in the mussel *Mytilus edulis*: kinetics and importance of uptake via food and sea water. Mar. Biol. 96: 349-353.

Roesijadi, G.. 1992. Metallothioneins in metal regulation and toxicity in aquatic animals. Aquat. Toxicol. 22: 81-114.

Tessier, A. Y. Couillard, P.G.C. Campbell and J.C. Auclair. 1993. Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve *Anodonta grandis*. Limnol. Oceanogr. 38(1): 1-17.

Tessier, A., P.G.C. Campbell, J.C. Auclair and M. Bisson. 1984. Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc *Elliptio complanata* in a mining area. Can. J. Fish. Aquat. Sci. 41: 1463-1472.

Thomann, R.V., J.D. Mahoney and R. Mueller. 1995. Steady-state model of biota sediment accumulation factor for metals in two marine bivalves. Environ. Toxicol. Chem. 14(11): 1989-1998.

Thompson, J.K. and F.H. Nichols. 1988. Food availability controls seasonal cycle of growth in *Macoma balthica* (L.) in San Francisco Bay, California. J. Exp. Mar. Biol. Ecol. 116: 43-61.

Timmermans, K.R.. 1993. Accumulation and effects of trace metals in freshwater invertebrates. In: Ecotoxicology of Metals in Invertebrates. R. Dallinger and P.S. Rainbow (Eds.). 133-148.

Vangenechten, J.H.D., S.R. Aston and S.W. Fowler. 1983. Uptake of americium-241 from two experimentally labelled deep sea sediments by three benthic species: a bivalve mollusc, a polychaete and an isopod. Mar. Ecol. Prog. Ser. 13: 219-228.

Viarengo, A., S. Palermo, G. Zanicchi, R. Capelli, R. Vaissiere and M. Orunesu. 1985. Role of metallothioneins in Cu and Cd accumulation and elimination in the gill and digestive gland cells of *Mytilus galloprovincialis* L.. Mar. Environ. Res. 16: 23-36.

Vlas, J. de. 1985. Secondary production by siphon generation in a tidal flat population of *Macoma balthica*. Neth. J. Sea Res. 19: 1147-164.

Vlas, J. de. 1979. Annual food intake by plaice and flounder in a tidal flat area in the Dutch Wadden Sea, with special reference to consumption of regenerating parts of macrobenthic prey. Neth. J. Sea Res. 13: 117-153.

Wang, W.-X. and N.S. Fisher. 1996. Assimilation of trace elements and carbon by the mussel *Mytilus edulis*: Effects of food composition. Limnol. Oceanogr. 41(2): 197-207.

Wang, W.-X., J.R. Reinfelder, B.-G. Lee and N.S. Fisher. 1996. Assimilation and regeneration of trace elements by marine copepods. Limnol. Oceanogr. 41(1): 70-81.

Wang, W.-X., N.S. Fisher and S.N. Luoma. 1995. Assimilation of trace elements ingested by the mussel *Mytilus edulis*: effects of algal food abundance. Mar. Ecol. Prog. Ser. 129: 165-176.

Widdows, J., P. Fieth and C.M. Worrall. 1979. Relationship between seston, available food and feeding activity in the common mussel *Mytilus edulis*. Mar. Biol. 50: 195-207.

Zwarts, L. and J. Wanink. 1989. Siphon size and burying depth in deposit- and suspension-feeding benthic bivalves. Mar. Biol. 100: 227-240.

CHAPTER 7: SUMMARY

This chapter summarizes the conclusions of this study and considers the implications with respect to a wider literature base. The importance of SPM in chemical transport (environmental association, behaviour and fate), metal monitoring (for geochemical reconnaissance or contaminant monitoring), and biological uptake is emphasized.

1.0 CONCLUSIONS

Suspended particulate matter (SPM; predominantly fine permanently suspended particles) collected at depositional environments in the mid-estuarine region of the Fraser River is significantly enriched in organic matter, iron oxides (reducible iron), manganese oxides (easily reducible manganese), and metals (Cd, Cu, Pb, Zn) over deposited sediment (DS) collected at the same locations. In SPM, the seasonal variation in these geochemical properties is significant over the course of a year, with maxima in organic matter and iron oxides occurring during winter months (Dec through Mar) when river discharge is lowest. The concentrations of Cd, Cu, Pb and Zn were often an order of magnitude higher in SPM than in DS, in a range expected to exert effects in natural systems (see section 3.0). Differences of this scale were most apparent in the easily reducible, reducible, and organic phases, but were much less apparent with residual metals which frequently did not differ between the two sediments. Copper and zinc partition in SPM differently than in DS, while no difference was found with lead. A higher proportion of copper and zinc partition to the leachable phases of SPM than in DS. While copper was found to partition predominantly into the easily reducible and organic phases, zinc was found to partition predominantly into the easily reducible phase. A higher proportion of copper partitioned to the easily reducible and organic phases in SPM than DS, and a higher proportion of zinc partitioned to the easily reducible phase of SPM than DS.

The seasonal differences in metal concentrations in SPM and DS were related to temporal changes in the measured physico-chemical and geochemical characteristics of the Fraser River Estuary. However, the two sediment types were best related to different variables, and different strengths of relationship were observed. Metal concentrations in SPM were more closely related to it's geochemical properties than DS. This was particularly true of the easily reducible and organic phases and less true of the residual phase which is essentially unreactive. Iron oxides (reducible iron), manganese oxides (easily reducible manganese) and organic content (loss on ignition; LOI) were the dominant correlates with metal levels in SPM, while pH and manganese oxides and organic content were the dominant correlates with metal levels in DS. Overall, it appears that SPM is an effective medium for developing and validating theory on the geochemical controls of metal behaviour.

The geochemical characteristics of SPM versus DS did not affect how spiked ^{109}Cd partitioned into the two sediments. They did, however, affect the extent of desorption of ^{109}Cd from the sediments. SPM, which contained significantly higher concentrations of iron and manganese oxides and more organic matter, did not release ^{109}Cd to the water to the same extent as DS. At environmentally realistic exposure concentrations (4.0 mg/kg dry wt. and 0.5 μg/L), assimilation efficiency of ^{109}Cd by littleneck clams (*Protothaca staminea*) was greater from SPM than DS (33% vs. 19-25%), but not significantly so. This observation suggests that the concentration of ^{109}Cd used was insufficient to saturate DS binding sites, and thus the sediments were essentially the same. This is manifest in the observation that the phase ratios in the two sediments were very similar and ^{109}Cd partitioning was the same. Uptake of ^{109}Cd to *P. staminea* and *Macoma balthica*, while a less effective estimate of bioavailability than assimilation, indicated that the particulate phase was the dominant uptake route in both organisms (79 - 91%) and uptake was related to desorption. Higher desorption of ^{109}Cd from particulates was indicative of an enhanced ability of organisms to take up ^{109}Cd from the particulate route. It appears that the desorption is a good predictor of the fraction of particle-associated ^{109}Cd that can be taken up by organisms.

Overall, the similar assimilation efficiencies measured from the two sediments when the same concentrations were used and the same partitioning was observed, coupled with the much higher metal concentrations in SPM than DS and a relative increased proportion of leachable metal, suggest that SPM is a relatively more potent vector of metal uptake to bivalves. The overall importance of SPM vs. DS is a product of concentration, partitioning, and assimilation determined in this study and the organism's relative exposure to the two. Some of these factors vary considerably over seasonal scales; put together, they indicate the importance of SPM as a metal bearing vector involved in the transfer of metals to organisms.

2.0 GEOCHEMICAL IMPLICATIONS

SPM is clearly an important metal-bearing vector in aquatic systems. This research has shown that, in comparison to deposited sediment, SPM represents a more concentrated pool of trace metals, with more of the metal in weakly bound phases. Due to the "geochemically labile" state of the SPM, it is an important material in controlling sorption, exchange and release reactions in the Fraser River Estuary. In addition, as the most concentrated metal load, it represents a key transport mechanism for metals, determining metal fate in the Fraser River Estuary. Knowledge of the high concentration of metals in SPM can also be applied to understanding the incidence of metal hotspots, and their causes (i.e., heavy sedimentation with little release).

This study has provided some important information that could only be determined over a longer-term field based study. A high observed variability is indicative of in-situ interactions of a number of physical, chemical, and geochemical variables acting upon the system. The influence of geochemistry upon metal levels was assessed in this complex environment and was consistent with theory. As noted by Horowitz (1991) in fluvial systems, iron oxides and organic matter appear to be the most important factors determining the variability in metal concentration. The observations herein may carry over to other aquatic systems (i.e., McKee et al., 1989). In the estuarine transition from river to marine systems, the interaction between physical characteristics and particle geochemistry control both waterborne and deposited metal levels. Metal concentrations in the water and sediment of the deltaic front and the Strait of Georgia will be influenced by SPM geochemistry.

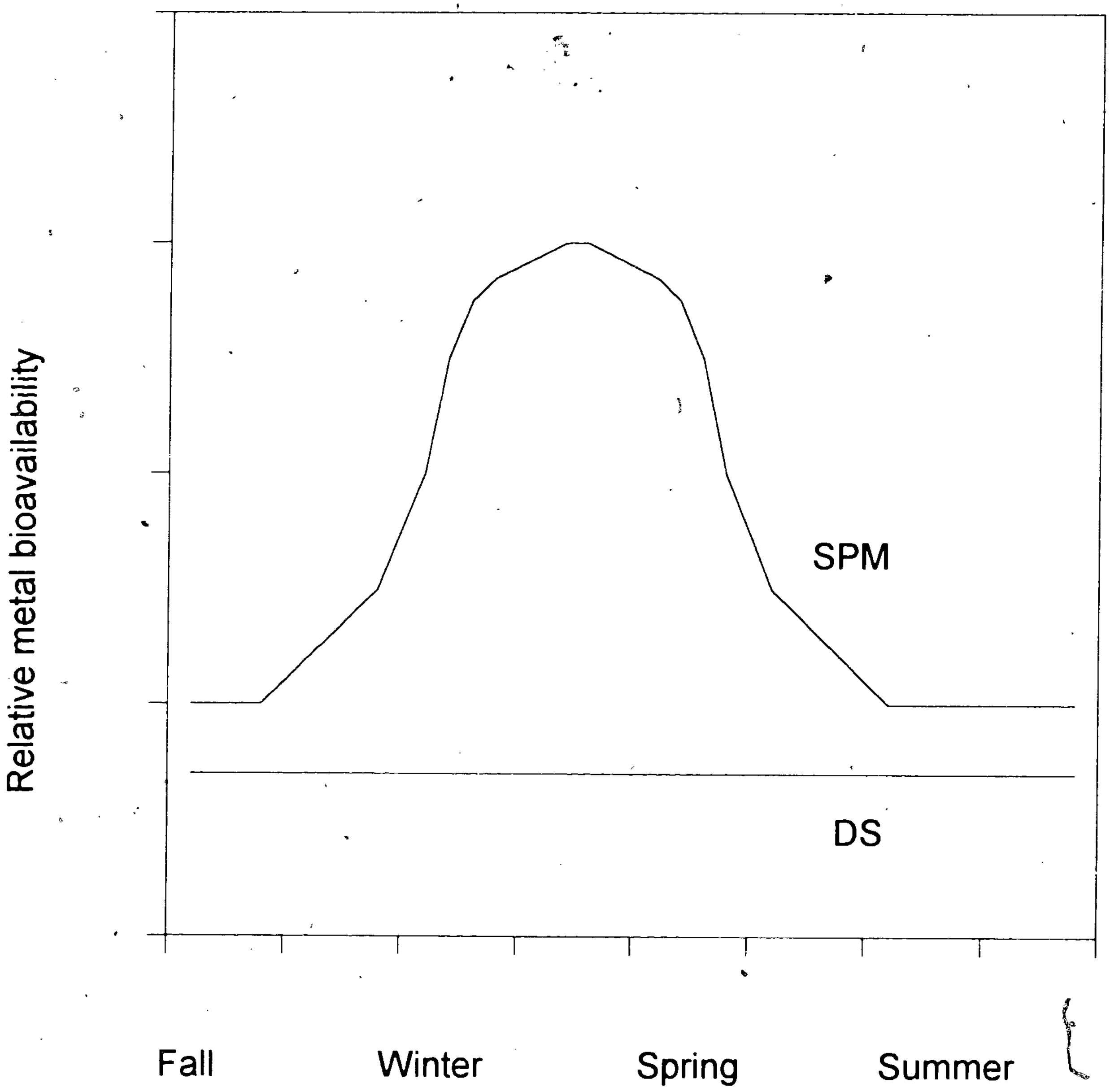
SPM represents a more concentrated pool of metals than DS in the Fraser River Estuary. SPM is quite uniform in particle size and may be a reflection of newer contaminant input, whereas the origins of DS are seldom understood. Therefore, for contaminant monitoring purposes, SPM is a more relevant material to sample than deposited sediment. SPM is variable in both volume and concentrations and must be considered in metal transport and concentration studies. SPM sampling along with water (filtered and unfiltered) would provide significant insight into contaminant association and fate processes than is currently being gained. In the frequently-studied Fraser River estuary this has seldom been considered.

3.0 BIOLOGICAL IMPLICATIONS

The geochemistry of SPM has important biological implications associated with the identification of risk of metal uptake. This research has shown that metal concentrations in SPM are very high relative to any other environmental compartment and have a definite seasonal component. It suggests that in concert with the high metal levels is a high lability. Thus, it suggests that bioavailability of metals from SPM is dynamic, fluctuating seasonally and may be highest in winter months. In contrast, the bioavailability of metals from DS appears to remain constant (Figure 7.1). In order to identify exposure patterns, this seasonality must be matched with seasonal behaviour of target organisms.

The biological relevance of the metal levels encountered in SPM of the Fraser River Estuary can be communicated by comparison with British Columbia sediment quality guidelines. Mean monthly metals (Cd, Cu, Pb and Zn) in the easily reducible phase of SPM are above LEL (lowest effect levels) from several months in 1994-1995. The LEL, established for total metal, represents a level of sediment contamination that can be tolerated by the majority of benthic organisms and represents the threshold at which ecotoxic effects become apparent (BCMOELP, 1994). Given the difference in biological accessibility between easily reducible and total metal, such concentrations could represent a significant risk to exposed organisms. On two occasions in the winter months (1995), copper in the easily reducible phase of SPM exceeded the severe effects level (SEL), the level at which pronounced disturbance of the sediment dwelling community can be expected, and a concentration that would be detrimental to the majority of benthic species in the sediment. Given the difference in biological accessibility between easily reducible and total metal, and the in-situ exposure to a mixture of metals, such concentrations are of significant concern and suggest that significant potential exists for biological effects upon exposure to SPM in the Fraser River Estuary.

Figure 7.1 Hypothetical seasonal fluctuation in metal bioavailability at study sites in the Fraser River Estuary



Organisms in contact with a more nutritious and contaminant laden food source (i.e., the high organic matter, high metal content SPM of December 1994 to March 1995), could take up more metal depending upon seasonal patterns of activity and the nature of the behavioral response to fluctuations in food quality (i.e., Taghon et al., 1978; Taghon and Jumars, 1984). By knowing the location and the organisms at greatest risk based upon SPM concentrations, metal partitioning, and knowledge gained in the availability of distinct phases, effective biological monitoring programs can be developed. Ongley et al. (1988) have concluded that water may be an inappropriate sampling medium for toxic chemical sensing in aquatic systems; they found SPM to be the most appropriate sampling medium. Important model organisms, *P. staminea* and *M. balthica* illustrate the potential biological importance of SPM as a route of metal uptake. The geochemical differences between SPM and DS may be most relevant to organisms such as *M. balthica*. *M. balthica* is able to filter food from the overlying water column while the inhalant siphon is just at the sediment surface (Brafield and Newell, 1961; Hummel, 1985). While deposit feeding the clam extends it's inhalant siphon over the sediment surface (Zwarts and Wanink, 1989) which may require reduction in the clam's burial depth. By shifting from deposit to suspension feeding *M. balthica* might be able to increase it's burial depth (Zwarts and Wanink, 1989; Lin and Hines, 1994), minimizing sublethal and lethal predation. However, this organism could also use behavioral switching to avoid high contaminant loads (i.e., a pulse in the contaminant loads of SPM). Thus, an optimal survival strategy would be a trade off between contaminant uptake and predation risk.

The ability of organisms to assimilate contaminants must be considered and is still not well understood. It is recognized as an important requirement for contaminants to exert effects via the gut pathway. To exert an effect, a contaminant must be bioavailable. The calculation of assimilation efficiency is a direct means of determining bioavailability. The determined AE of 33% from SPM suggests that organisms can pick up significant metal loads from the ingestion of SPM. This is confirmed in consideration of simple uptake where 79 - 91% of isotope burden was from the particulate route. The accumulation of pollutants in sediment-dwelling bivalves appears to depend mainly upon the natural behaviour and physiology of the organism (Absil et al., 1996), such as the ability of bivalves to modify digestive processing to reduce exposure to high, biologically available metal concentrations (Decho and Luoma, 1996). A possible corollary to this is the potential for nutritional deficits as a secondary effect of ingesting contaminated food (Decho and Luoma, 1996).

This work emphasises the importance of SPM in controlling the behaviour, fate and uptake of metals in aquatic systems and the importance of both geochemical and biological processes and their interaction in determining the uptake of metals. In order to protect aquatic organisms involved in detritus feeding, initiatives must consider the contaminant load of SPM and it's availability.

4.0 REFERENCES

Absil, M.C.P., M. Berntssen and L.J.A. Gerringa. 1996. The influence of sediment, food and organic ligands on the uptake of copper by sediment-dwelling bivalves. Aquat. Toxicol. 34: 13-29.

BCMOELP, 1994. Approved and working criteria for water quality -1994. Table 1b, Approved and working criteria for sediment quality. British Columbia Ministry of Environment, Lands and Parks. February, 1994.

Brafield, A.E. and G.E. Newell. 1961. The behaviour of Macoma balthica (L.). J. Mar. Biol. Assoc. UK. 41: 81-87.

Decho, A.W. and S.N. Luoma. 1996. Flexible digestion strategies and trace metal assimilation in marine bivalves. Limnol. Oceanogr. 41(3): 568-572.

Horowitz, A.J.. 1991. A primer on sediment trace-element chemistry. Second Edition, Lewis Publishers, Chelsea, Michigan. 136 pp.

Hummel, H.. 1985. Food intake of *Macoma balthica* (Mollusca) in relation to seasonal changes in it's potential food on a tidal mudflat in the Dutch Wadden Sea. Neth. J. Sea Res. 19: 52-76.

Lin, J. and A.H. Hines. 1994. Effects of suspended food availability on the feeding mode and burial depth of the Baltic clam, *Macoma balthica*. Oikos 69: 28-36.

McKee, J.D., T.P. Wilson, D.T. Long and R.M. Owen. 1989. Geochemical partitioning of Pb, Zn, Cu, Fe and Mn accross the sediment-water interface in large lakes. J. Great Lakes Res. 15(1): 46-59.

Ongley, E.D., D.A. Birkholz, J.H. Carey and M.R. Samoiloff. 1988. Is water a relevant sampling medium for toxic chemicals? An alternative environmental sensing strategy. J. Environ. Qual. 17(3): 391-401.

Taghon, G.L. and P.A. Jumars. 1984. Variable ingestion rate and it's role in optimal foraging behaviour of marine deposit feeders. Ecology 65: 549-558.

Taghon, G.L., R.F.L. Self and P.A. Jumars. 1978. Predicting particle selection by deposit-feeders: a model and prediction. Limnol. Oceanogr. 23: 752-759.

Zwarts, L. and J. Wanink. 1989. Siphon size and burying depth in deposit- and suspension-feeding benthic bivalves. Mar. Biol. 100: 227-240.

APPENDIX I: DEFINITIONS AND ABBREVIATIONS

AAS	atomic absorption spectrophotometry; the method used for the detection of metals in this study
absorbtion (biological)	uptake and transport of an element across the gut (or other environmental interface) into the internal environment of an organism
absorbtion (chemical)	the incorporation of matter into a matrix (i.e., a hydrophobic chemical into octanol)
adsorption	the accumulation of matter at the solid-water interface
assimilation	uptake and transport of an element across the gut (or other environmental interface) into the internal environment of an organism and incorporation of an element in structural or metabolic machinery
assimilation efficiency	the efficiency with which an element of interest is retained by an organism relative to an inert tracer with a similar gut passage time as determined by the twin tracer method of Fisher and Reinfelder (1991)
BCMOELP	British Columbia Ministry of Environment, Lands and Parks
bioavailability	exposure and uptake, an estimate of the capacity of a metal to end up in an organism, regardless of whether it subsequently reacts with metabolic machinery
colloids	submicron particles generated by physical fragmentation and erosion and by precipitation from oversaturated solutions. Colloids are present in relatively high concentrations in natural waters and are surface reactive due to their high surface areas
coordination compound	a compound formed in which the atoms, molecules or ions involved improve their stability by changing their relationships with another atom, molecule or ion
DS	deposited sediment; sedimentary material in/on which benthic organisms live

desorption	the release of metal sorbed to particulate matter to the water
dissolved metals	metals present in ionic form. Operationally, the < 0.45 µm fraction of metals is considered to be dissolved.
easily reducible metal	operationally defined as metal extracted from sediment with 0.1 N $NH_2OH\cdot HCl$ in 0.01 N HNO_3 for 0.5 h
EDTA	ethylenediaminetetraacetic acid; a metal chelating agent
FAAS	atomic absorption spectrophotometry in which an air acetylene flame is the means of atomization
GESAMP	the International Maritime Organization/Food and Agriculture Organization/United Nations Educational Scientific and Cultural Organization/World Meteorological Organization/World Health Organization/International Atomic Energy Agency/United Nations/United Nation Environment Programme Group of Experts on the Scientific Aspects of Marine Pollution
GFAAS	atomic absorption spectrophotometry in which a graphite furnace is the means of atomization
hydrogenic	formed in water
hysteresis	the response of the particle concentration of a water body to change (in hydrographic conditions) being dependent upon previous responses to change
iron oxides	operationally defined as iron extracted from sediment with 0.1 N $NH_2OH\cdot HCl$ in 25% HOAc at 95°C for 6h. This group of compounds consists of Fe, O, and/or OH and can differ in composition, valence of Fe and crystal structure. Iron oxides are important materials that scavenge metals in aquatic systems
K_d	partition coefficient; (sediment bound metal [mg/kg])/(dissolved metal [mg/L])

labile	a material (i.e., metal) in a form that is available for chemical and biological interactions
leachable	operationally defined as the sum of metal extracted by three weak extractants used in this study (0.1 N $NH_2OH{\cdot}HCl$ in 0.01 N HNO_3; 0.1 N $NH_2OH{\cdot}HCl$ in 25% HOAc; and NH_4OH)
LEL	lowest effect level, the level of sediment contamination that can be tolerated by the majority of benthic organisms, and at which actual ecotoxic effects become apparent
ligands	the anions or molecules with which a metal ion can form a coordination compound
lithogenic	formed in the earth (mineral)
LOI	loss on ignition; a measure of the organic content of a sediment
manganese oxides	operationally defined as manganese extracted from sediment with 0.1 N $NH_2OH{\cdot}HCl$ in 0.01 N HNO_3 for 0.5h. This group of compounds consists of Mn, O, and/or OH and can differ in composition, valence of Mn and crystal structure. Manganese oxides are important materials that scavenge metals in aquatic systems
NRCC	National Research Council of Canada
organic metal	operationally defined as metal extracted from sediment with 1 N NH_4OH for 1wk
partitioning	the distribution of an element among the various possible forms
reducible metal	operationally defined as metal extracted from sediment with 0.1 N $NH_2OH{\cdot}HCl$ in 25% HOAc at 95°C for 6 h from which is subtracted the easily reducible metal

residual metal	operationally defined as metal extracted from sediment with a 3:1 mixture of conc HCl and conc HNO_3, from which is subtracted the metal extracted by the three other extractions (easily reducible, reducible, and organic metal)
SEL	severe effect level, the level at which pronounced disturbance of the sediment dwelling community can be expected. This is the concentration of a compound that would be detrimental to the majority of benthic species in the sediment.
selective extraction	an extraction that is operationally defined, but designed to selectively extract the components of a specific sediment phase (i.e., manganese oxides)
sorption	a general term that describes the accumulation of matter at the solid-water interface or incorporation into the solid matrix by any process (i.e., ion exchange, electrostatic attraction, precipitation)
speciation	the chemical forms in which an element exists in water
SPM	suspended particulate matter; particulate material in the water column to which benthic organisms can be exposed through filter feeding and as particles settle
surface complexation	the formation of coordinative bonds at a particle surface
uptake	the active movement of an element or material from the external environment to the internal environment by an organism

APPENDIX II: METAL ANALYSIS CONDITIONS AND QA/QC

Metal Analysis Conditions

Cadmium

Cadmium was determined at a wavelength of 228.8 mμ using a Perkin Elmer 4100 ZL graphite furnace AAS. Sample was injected into the furnace followed by a drying step, pyrolysis and atomization. A stock solution of 1020 μg/ml (ppm) (Sigma Chemical Company) was used for preparation of standards. The detection limit of this method for the GFAAS was 0.2 μg/L. At the solid to extractant ratios used (1:15 wet) and the mean dry/wet ratios (approximately 50%), this translates to detection limits of approximately 5.0 μg/kg dry weight.

Copper

Copper was determined at a wavelength of 324.7 mμ using flame AAS with direct aspiration of the aqueous solution into the flame. A stock solution of 1015 μg/ml (ppm) (Sigma Chemical Company) was used for the preparation of standards. The detection limit for copper was 10 μg/L in dilute acid (250 μg/kg dry weight), and samples were seldom near these limits. For NH_4OH extracts, sample concentrations were always well above detection.

Iron

Iron was determined at a wavelength of 248.3 mμ with flame AAS with direct aspiration of the aqueous solution into the flame. A stock solution of 1040 μg/ml (ppm) (Sigma Chemical Company) was used for preparation of standards. For iron, dilution to 1/10 was necessary for the easily reducible and reducible extracts; with a dilution of up to 1/100 necessary for the aqua regia digest (and occasional reducibles) to bring concentrations to within the linear range. All sample iron concentrations were well above detection.

Lead

Lead was determined at a wavelength of 217.0 mμ using a flame AAS by direct aspiration of the aqueous solution into the flame. A stock solution of 1020 μg/ml (ppm) (Sigma Chemical Company) was used for preparation of standards. The detection limit of this method for the FAAS was 10 μg/L in dilute acid (250 μg/kg dry weight), and approximately 100 μg/L in NH_4OH (2.5 mg/kg dry weight).

Manganese

Manganese was determined at a wavelength of 279.4 mμ by flame AAS with direct aspiration of the aqueous solution into the flame. A stock solution of 1010 μg/ml (ppm) (Sigma Chemical Company) was used for preparation of standards. For manganese, dilution to 1/10 was usually necessary for the easily reducible, reducible and aqua regia extracts to bring concentrations to within the linear range. All manganese concentrations were well above detection.

Zinc

Zinc was determined by flame AAS at a wavelength of 214.0 mμ by flame AAS with direct aspiration of the aqueous solution into the flame. Stock solution of 1040 μg/ml (ppm) (Sigma Chemical Company) was used for preparation of standards. Most of the sample zinc concentrations were well above detection. The detection limit of this method for the FAAS was 3 μg/L in dilute acid (75 μg/kg dry weight), and approximately 20 μg/L in NH_4OH (500 μg/kg dry weight).

QA/QC

Mean and SE of NRCC MESS-2 reference sediment in each phase. The number of samples analyzed was 15 for all metals but cadmium (n=5). Note that certified values for these extractions are not available, rather reference sediment was used to ensure data consistency.

Metal	0.1N $NH_2OH{\cdot}HCl$ in 0.01 N HNO_3 for 0.5h Mean ± SE (mg/kg)	0.1N $NH_2OH{\cdot}HCl$ in 25% HOAc at 95°C for 6h Mean ± SE (mg/kg)	1 N NH_4OH for 1 week Mean ± SE (mg/kg)	3:1 conc. HCl and HNO_3 at 70°C for 8h Mean ± SE (mg/kg)	NRCC Certified Total (Strong Acid Digestion) Mean ± 95% CI (mg/kg)
Cd	0.274 ± 0.23	0.341 ± 0.40	bd	na	0.24 ± 0.01
Cu	bd	4.61 ± 0.30	3.19 ± 0.20	30.77 ± 0.90	39.3 ± 2.0
Fe	164 ± 12	6441 ± 842	22.6 ± 1.9	25261 ± 1018	-
Mn	52.6 ± 1.7	166 ± 11	0.72 ± 0.08	366 ± 10	-
Pb	bd	6.48 ± 0.52	bd	16.2 ± 1.1	21.9 ± 1.2
Zn	5.52 ± 0.20	47.3 ± 3.8	3.48 ± 0.52	143 ± 3.7	172 ± 16

* bd = below detection
na = not analyzed
- = not available

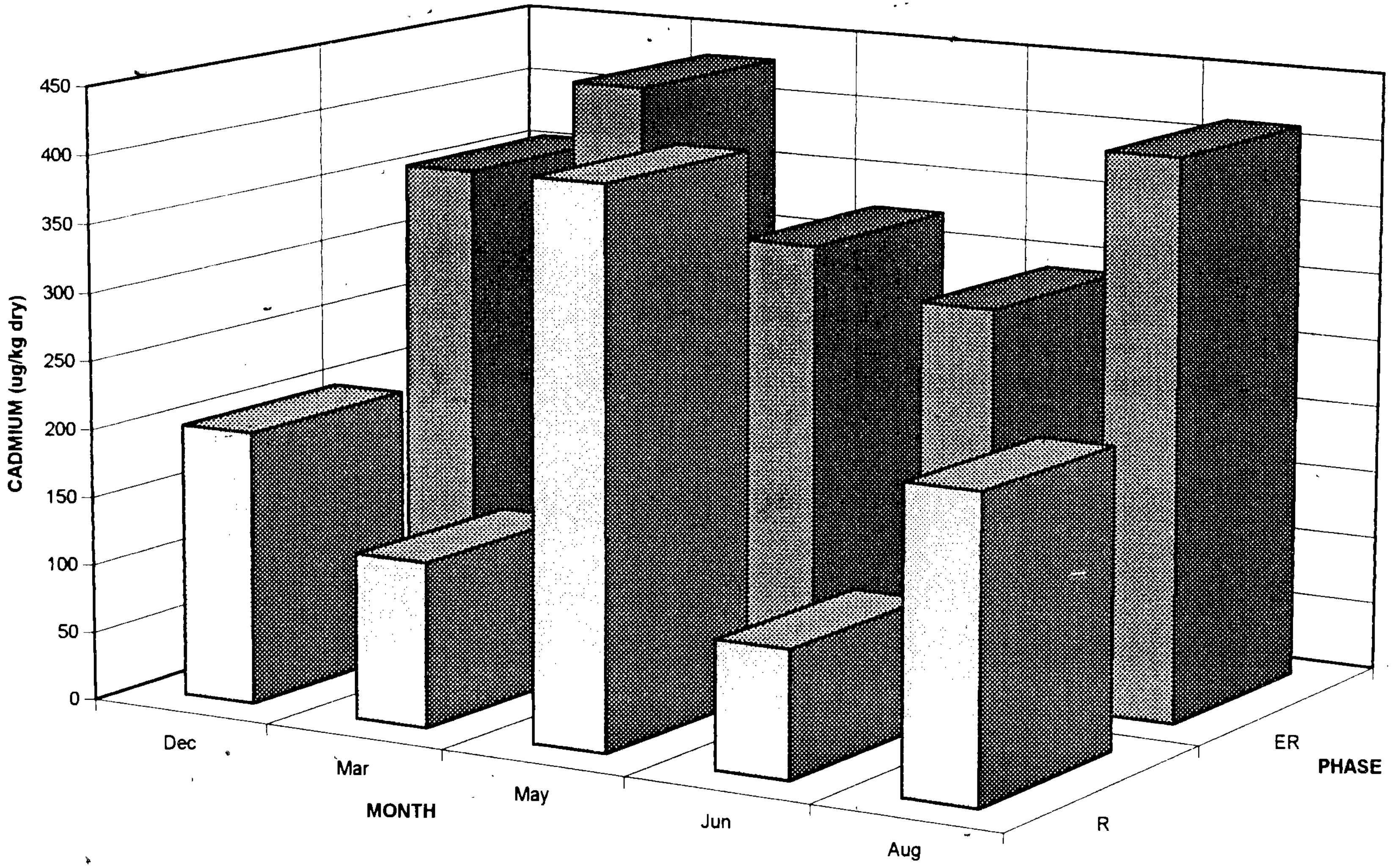
All values appear to be within acceptable ranges and variability, with the possible exception of cadmium, which appears to overestimate the values slightly. The only comparison possible is Fe_2O_3 content with iron in the (BDH Analar) 0.1N $NH_2OH{\cdot}HCl$ in 25% HOAc minus the iron in (BDH Analar) 0.1N $NH_2OH{\cdot}HCl$ in 0.01 N HNO_3 which yields a value of 6.28% versus the certified value of 6.22 ± 0.31%.

APPENDIX III: METAL CONCENTRATIONS IN SPM AND DS BY MONTH

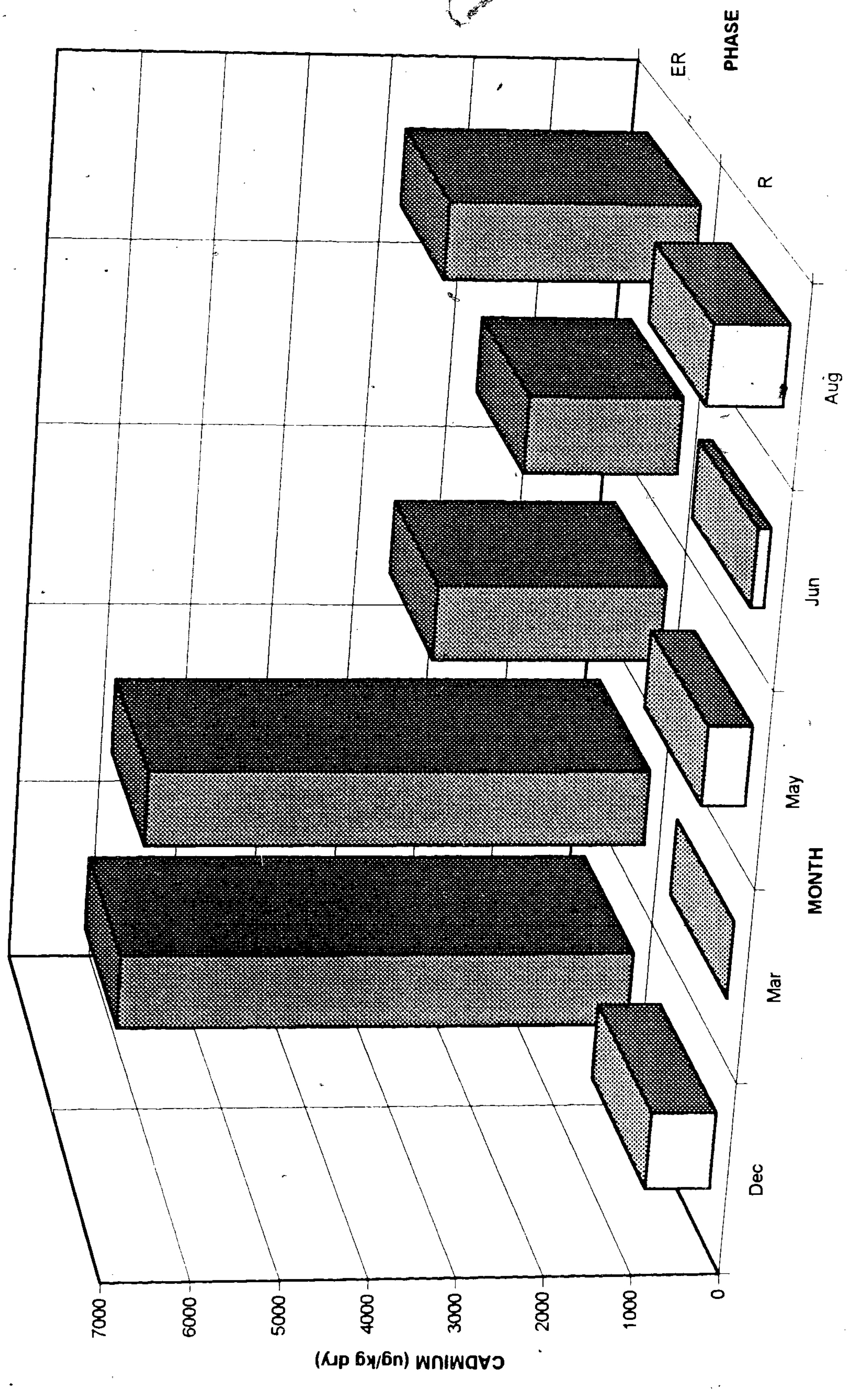
Metal	Sediment	Month	Easily Reducible			Reducible			Organic			Residual		
			Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N
Cadmium	Deposited	Dec 94	0.355	0.015	8	0.200	0.140	9	bd	bd	bd	na	na	na
(mg/kg dry)		Mar 95	0.430	0.050	9	0.120	0.050	9	bd	bd	bd	na	na	na
		May 95	0.320	0.050	9	0.405	0.950	8	bd	bd	bd	na	na	na
LEL - 0.6		Jun 95	0.290	0.030	9	0.090	0.400	9	bd	bd	bd	na	na	na
SEL = 10		Aug 95	0.410	0.055	7	0.220	0.130	9	bd	bd	bd	na	na	na
	Suspended	Dec 94	6.18	1.61	9	0.735	1.31	8	bd	bd	bd	na	na	na
		Mar 95	5.98	2.85	9	-2.06	1.96	9	bd	bd	bd	na	na	na
		May 95	2.71	0.33	9	0.495	0.180	9	bd	bd	bd	na	na	na
		Jun 95	1.80	0.19	9	0.145	0.250	9	bd	bd	bd	na	na	na
		Aug 95	2.91	0.44	9	0.845	0.242	9	bd	bd	bd	na	na	na
Copper	Deposited	Aug 94	8.20	1.49	9	-1.84	0.99	9	2.02	0.82	8	22.0	3.3	9
(mg/kg dry)		Sep 94	6.83	0.36	9	-1.61	0.91	9	2.37	0.43	9	17.2	1.7	7
		Oct 94	5.81	0.38	3	1.89	0.16	3	1.40	0.14	3	17.2	0.3	2
LEL = 16		Nov 94	8.77	0.33	9	1.45	0.40	9	4.15	0.70	9	17.0	0.7	9
SEL = 110		Dec 94	5.07	0.79	9	2.70	1.10	9	2.62	0.88	8	18.2	1.5	9
		Jan 95	10.9	1.62	9	-3.16	1.12	9	4.27	0.57	9	13.1	1.5	9
		Mar 95	2.52	0.35	9	6.55	0.62	9	5.68	1.22	9	14.3	7.5	9
		Apr 95	1.97	0.23	9	7.10	0.27	9	7.17	1.45	9	12.1	0.9	9
		May 95	2.07	0.44	9	5.96	0.37	9	6.87	0.82	9	18.3	2.1	9
		Jun 95	0.67	0.15	9	8.60	1.09	9	5.81	0.91	9	19.2	1.9	9
		Jul 95	1.40	0.18	9	7.01	0.81	9	5.15	0.44	9	17.5	1.6	9
		Aug 95	2.01	0.17	9	7.05	0.60	9	5.84	0.51	9	23.6	2.2	9
	Suspended	Aug 94			0	54.4	22.0	3	7.1	2.4	3	35.8	38.9	2
		Sep 94	26.8	6.2	3	14.2	6.3	3	8.2	1.7	3	33.4	7.4	3
		Oct 94	16.1	2.2	3	23.3	16.8	3			0	7.1	19.1	3
		Nov 94	97.2	65.1	3	-5.4	46.5	3	42.4	6.1	3	-13.7	10.3	3
		Dec 94	48.6	5.0	9	8.1	7.8	9	26.1	4.9	9	18.2	10.7	9
		Jan 95	141.1	27.9	9	-36.7	11.6	9	101.3	14.7	9	3.3	12.5	9
		Mar 95	131.6	73.7	9	27.7	6.0	9	139.3	56.6	9	139.6	73.0	9
		Apr 95	7.7	2.9	9	15.8	3.4	9	24.3	5.5	9	6.6	2.8	9
		May 95	6.2	1.5	9	15.6	2.5	9	19.1	3.4	9	27.4	6.3	8
		Jun 95	2.2	0.7	9	22.3	1.8	9	10.8	1.3	9	30.2	6.0	9
		Jul 95	7.0	1.4	9	17.6	4.9	9	26.9	5.7	9	9.9	5.0	8
		Aug 95	6.7	1.4	9	17.6	1.7	9	22.1	2.8	9	16.7	4.8	9
Iron	Deposited	Aug 94	2130	1102	9	2380	1437	9	33	23.0	9	20000	1070	9
(mg/kg dry)		Sep 94	830	199	9	4000	352	9	19	6.0	9	25900	1780	8
		Oct 94	1170	352	3	2950	326	3	34	5.8	3	20300	3160	3
		Nov 94	1090	129	9	5670	585	9	41	11.7	9	15700	940	8
		Dec 94	1360	274	9	5670	745	9	31	11.0	9	9600	3580	9
		Jan 95	1510	147	9	6040	233	9	100	17.3	9	15500	1560	9
		Mar 95	480	56	9	7640	579	9	79	27.3	9	16800	720	9
		Apr 95	490	31	9	5820	218	9	86	21.3	9	18000	1100	9
		May 95	430	13	9	5500	332	8	64	14.7	9	21600	1250	9
		Jun 95	570	72	9	5700	404	9	24	1.9	9	19000	850	9
		Jul 95	650	68	9	4060	365	9	40	5.0	9	20300	1220	9
		Aug 95	540	44	9	5120	286	9	30	3.2	9	25400	1580	8
	Suspended	Aug 94			0	7710	1240	3	16	11	3	35900	29500	3
		Sep 94	1730	163	3	6840	106	3	217	170	2	37600	4600	3
		Oct 94	1970	735	3	9070	4050	3	23		1	14500	5980	3
		Nov 94	8130	2810	3	33900	12000	3	1130	480	3	15200	8870	3
		Dec 94	6270	1790	9	22900	6200	9	1250	640	7	30800	6820	7
		Jan 95	8090	1430	9	45000	8190	9	2470	340	9	26000	6660	9
		Mar 95	2230	814	9	35800	9140	9	1240	230	9	17500	2520	9
		Apr 95	520	95	9	10600	2230	9	423	83	9	19600	3090	9
		May 95	470	49	9	7250	460	9	68	17	9	27500	2120	9
		Jun 95	295	44	9	7280	410	9	29	4	9	27400	1270	9
		Jul 95	730	92	9	6670	970	9	114	29	9	26500	3000	8
		Aug 95	600	62	9	8680	720	9	109	32	9	31200	2330	9

Metal	Sediment	Month	Easily Reducible			Reducible			Organic			Residual		
			Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N	Mean (mg/kg)	SE (mg/kg)	N
Lead	Deposited	Aug 94	1.6	0.5	9	2.1	0.4	9	bd	bd	bd	1.4	0.5	9
(mg/kg dry)		Sep 94	1.3	0.4	8	0.5	0.2	9	bd	bd	bd	4.8	2.7	8
		Oct 94	3.4	0.4	3	-0.3	0.9	3	bd	bd	bd	-0.5	3.2	3
LEL = 31		Nov 94	4.3	0.4	9	0.7	0.4	9	bd	bd	bd	3.6	0.4	8
SEL = 250		Dec 94	3.1	0.4	9	2.2	0.4	9	bd	bd	bd	3.3	0.5	9
		Jan 95	3.2	0.2	9	0.5	0.2	9	bd	bd	bd	2.0	0.6	9
		Mar 95	0.3	0.1	9	3.8	0.4	9	bd	bd	bd	2.9	0.7	9
		Apr 95	0.4	0.02	2	3.6	0.2	9	bd	bd	bd	0.6	0.2	9
	Suspended	Aug 94				18.2	5.6	3	bd	bd	bd	-9.4	3.5	3
		Sep 94	7.5	0.9	3	9.6	5.6	3	bd	bd	bd	9.2	3.7	2
		Oct 94	18.8	3.4	3	5.8	7.3	3	bd	bd	bd	-3.8	10.3	3
		Nov 94	61.6	16.1	3	-4.9	9.6	3	bd	bd	bd	4.8	2.2	3
		Dec 94	29.8	4.4	9	6.7	5.4	9	bd	bd	bd	8.8	3.6	9
		Jan 95	49.4	6.9	9	1.9	6.5	9	bd	bd	bd	31.5	10.8	9
		Mar 95	11.9	7.3	9	19.5	3.2	9	bd	bd	bd	2.0	8.0	8
		Apr 95	0.4	0.1	9	7.3	1.0	9	bd	bd	bd	3.3	1.7	9
Manganese	Deposited	Aug 94	31	11.9	8	245	32.7	9	20.6	11.0	8	88	112	9
(mg/kg dry)		Sep 94	80	15.5	9	80	17.4	9	11.4	2.6	6	277	83	8
		Oct 94	56	7.6	3	100	20.6	3	22.8	0.7	3	338	61	3
		Nov 94	119	25.4	9	96	19.2	9	11.2	1.9	9	378	123	8
		Dec 94	75	9.2	9	146	20.3	9	15.5	5.1	9	150	46	9
		Jan 95	96	12.7	9	301	33	9	11.7	2.8	9	403	39	9
		Mar 95	66	16.5	9	276	35.7	9	33.0	7.7	9	386	39	9
		Apr 95	106	6.6	9	244	18.7	9	46.0	11.8	9	422	44	9
		May 95	117	25.0	9	217	24	9	40.0	6.3	9	511	43	9
		Jun 95	91	12.7	9	196	27.7	9	25.6	3.4	9	529	40	9
		Jul 95	125	11.0	9	183	11.6	9	24.5	6.2	9	563	42	9
		Aug 95	184	20.6	9	164	21.6	9	12.7	2.1	6	740	77	9
	Suspended	Aug 94			0	461	92	3	12.3		1	625	789	3
		Sep 94	157	19.6	3	215	32	3	86.1	78.6	2	581	92	3
		Oct 94	244	70.4	3	207	173	3	12.1	9.1	2	212	206	3
		Nov 94	346	124.0	3	335	60	3	93.7	15.8	3	-191	334	3
		Dec 94	147	23.3	9	278	49	9	63.3	10	9	-104	142	7
		Jan 95	383	53.7	9	812	130	9	116	24.1	9	1550	395	9
		Mar 95	184	96.0	9	522	56	9	458	71.1	9	445	119	9
		Apr 95	140	8.6	9	373	41	9	358	63.7	8	219	71	9
		May 95	354	31.8	9	464	55	9	131	34.3	9	954	190	9
		Jun 95	123	21.5	9	353	32	9	28.1	4	9	874	123	9
		Jul 95	301	44.3	9	370	56	9	71	17.3	9	1030	208	8
		Aug 95	293	34.3	9	421	37	9	71.3	23.1	9	1020	130	9
Zinc	Deposited	Oct 94	8.83	0.6	3	4.4	1.5	3	15.3	11.0	3	55.2	9.6	3
(mg/kg dry)		Nov 94	7.94	0.5	9	10.4	1.1	9	15.2	6.2	9	52.3	5.2	8
		Dec 94	17.3	8.2	9	10.8	1.3	9	2.7	1.1	9	49.3	2.0	9
LEL = 120		Jan 95	8.60	0.5	9	11.4	1.3	9	19.9	5.8	9	33.6	9.0	9
SEL = 820		Mar 95	4.10	0.5	9	17.9	1.5	9	14.8	3.3	9	37.6	4.5	9
		Apr 95	5.11	0.4	9	16.1	1.1	9	18.1	7.4	9	23.9	7.5	9
		May 95	17.8	9.7	9	-0.2	9.3	9	15.3	5.5	9	18.2	8.0	9
		Jun 95	7.27	0.6	9	16.5	2.6	9	10.6	2.2	9	49.4	5.1	9
		Jul 95	3.08	0.3	9	18.5	2.5	9	23.0	8.4	9	36.5	12.3	9
		Aug 95	4.51	1.3	9	18.5	1.6	9	47.3	19.9	9	12.2	21.2	9
	Suspended	Oct 94	141	16	3	-15.7	30.8	3	11.0		1	5.1	31	3
		Nov 94	686	480	3	-373	431	3	171	15	3	-68	115	2
		Dec 94	211	41	9	16.8	46.3	9	80	28.6	9	-21	34	9
		Jan 95	488	124	9	-155	104	9	607	160	9	-221	175	9
		Mar 95	192	84	9	62.6	16.6	9	176	65	9	-134	85	9
		Apr 95	59	6	9	29.4	6.2	9	33.7	11.2	9	23	26	9
		May 95	71	18	9	38.7	8.4	9	53	19.5	9	-13	21	9
		Jun 95	44	4	9	38.8	3.5	9	7.8	1.5	9	103	8.8	9
		Jul 95	80	13	9	47.1	14.6	9	70.1	32.3	9	28	42	8
		Aug 95	68	7	9	47.9	3.3	9	24.4	2.8	9	58	6.3	9

CADMIUM IN DEPOSITED SEDIMENT



CADMIUM IN SUSPENDED PARTICULATE MATTER



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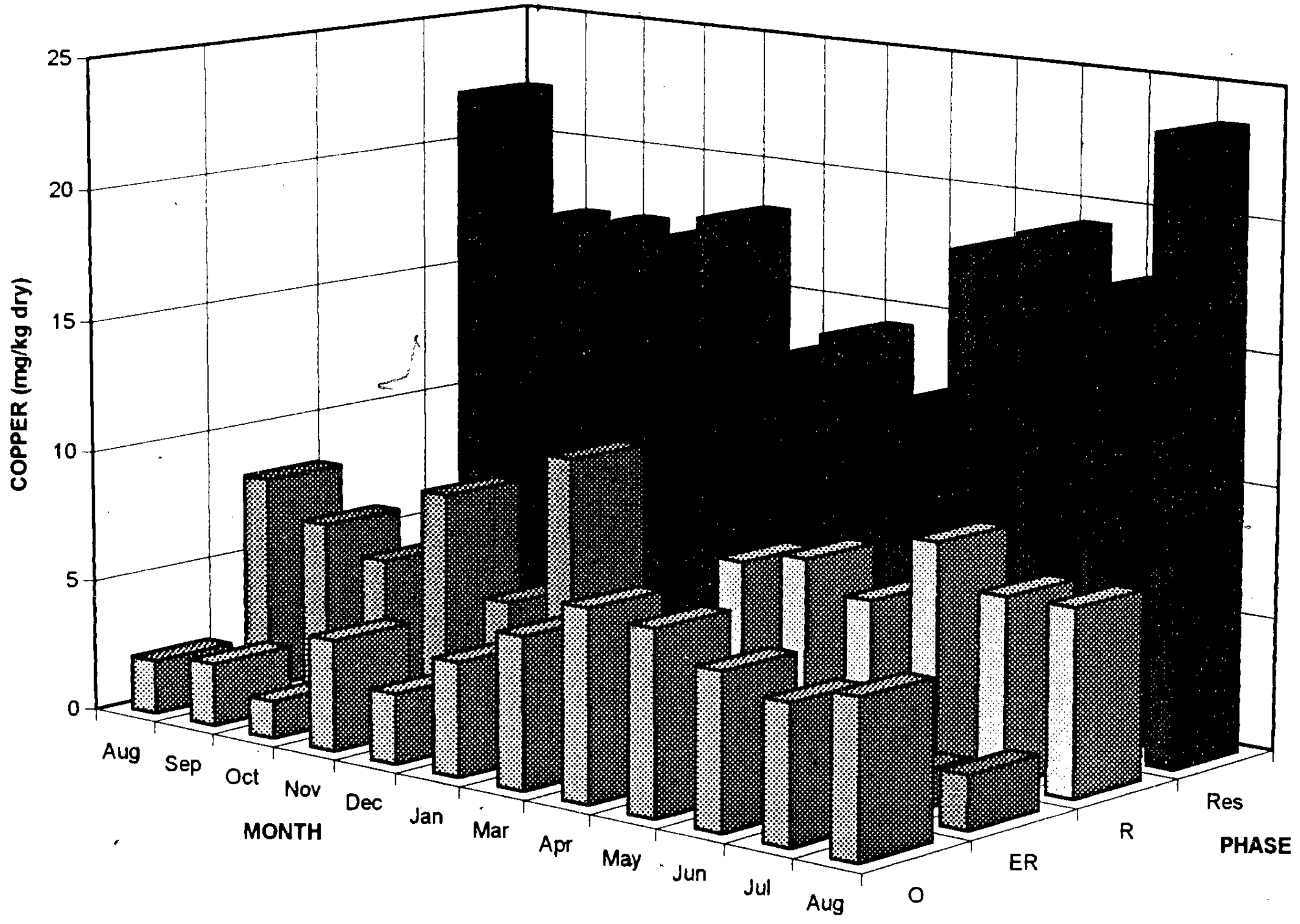

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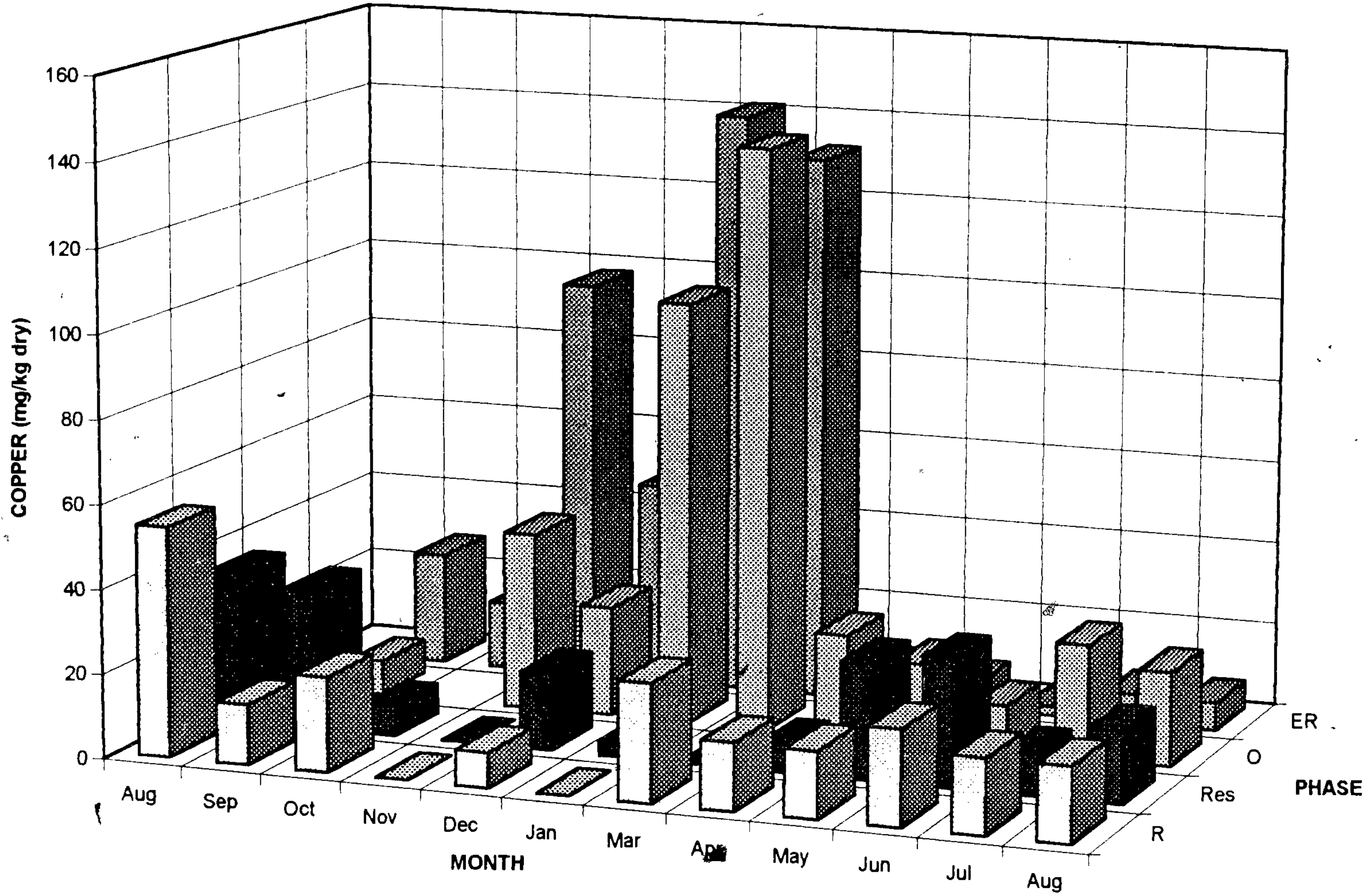
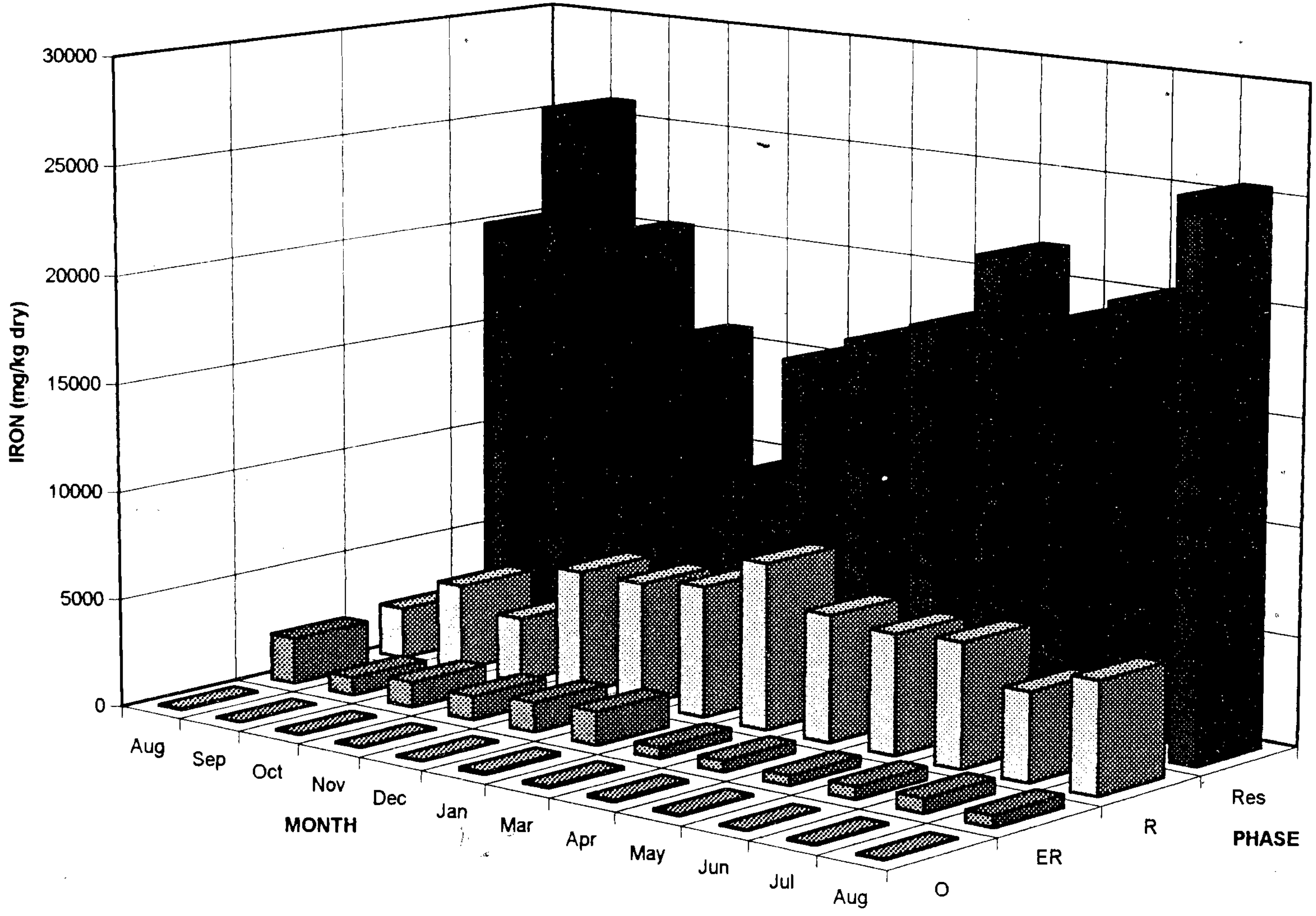
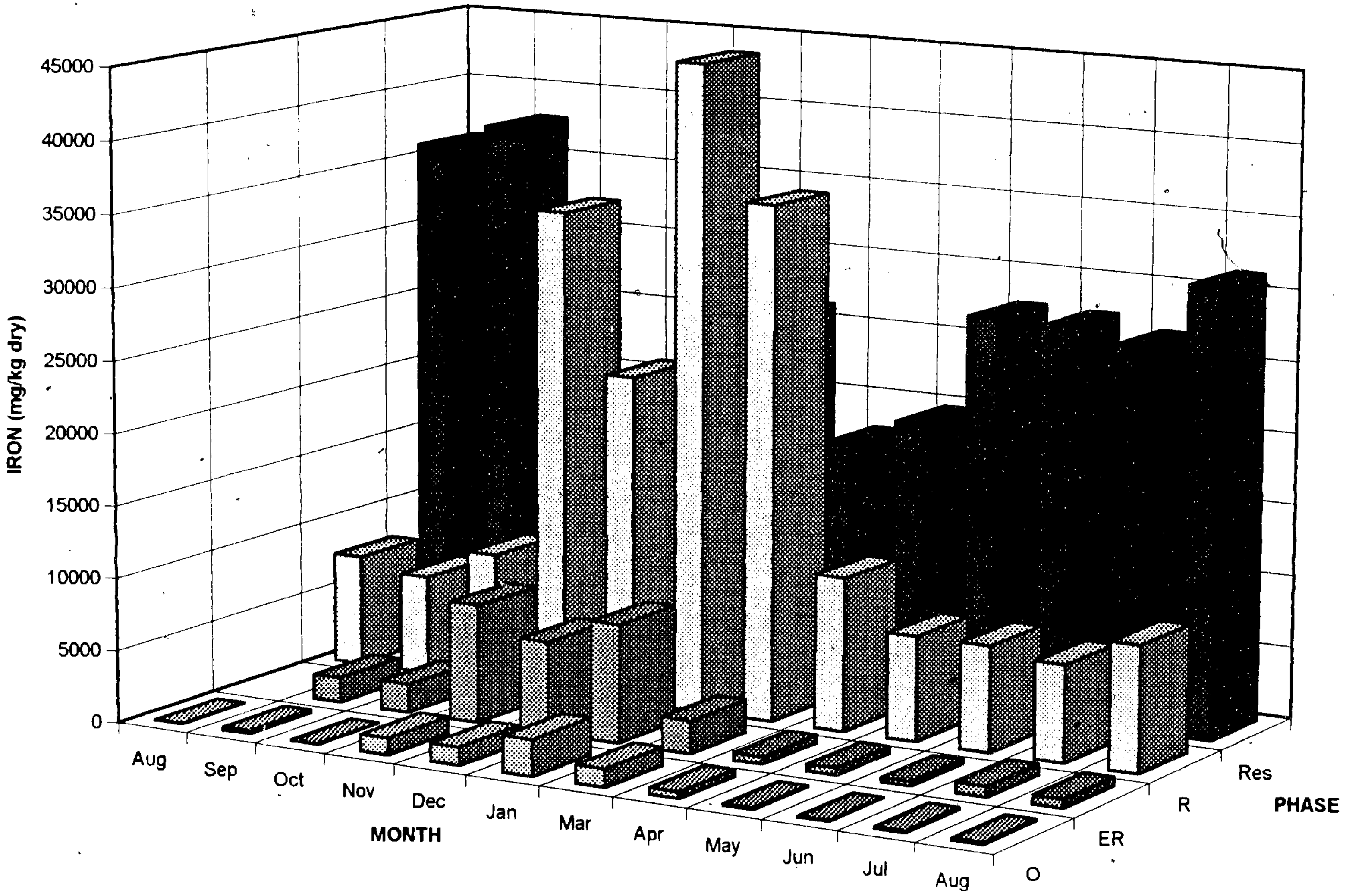




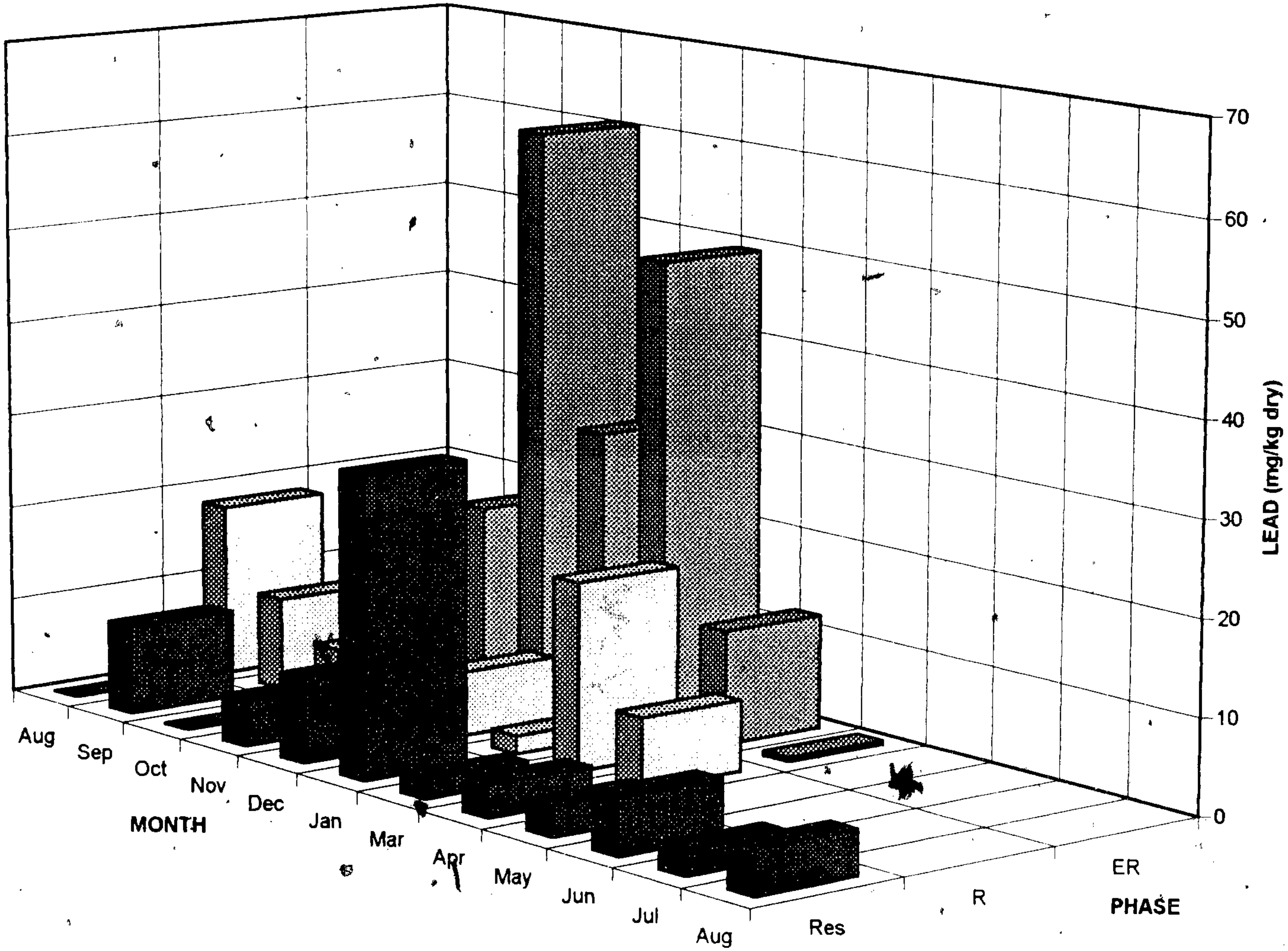
IRON IN DEPOSITED SEDIMENT

IRON IN SUSPENDED PARTICULATE MATTER

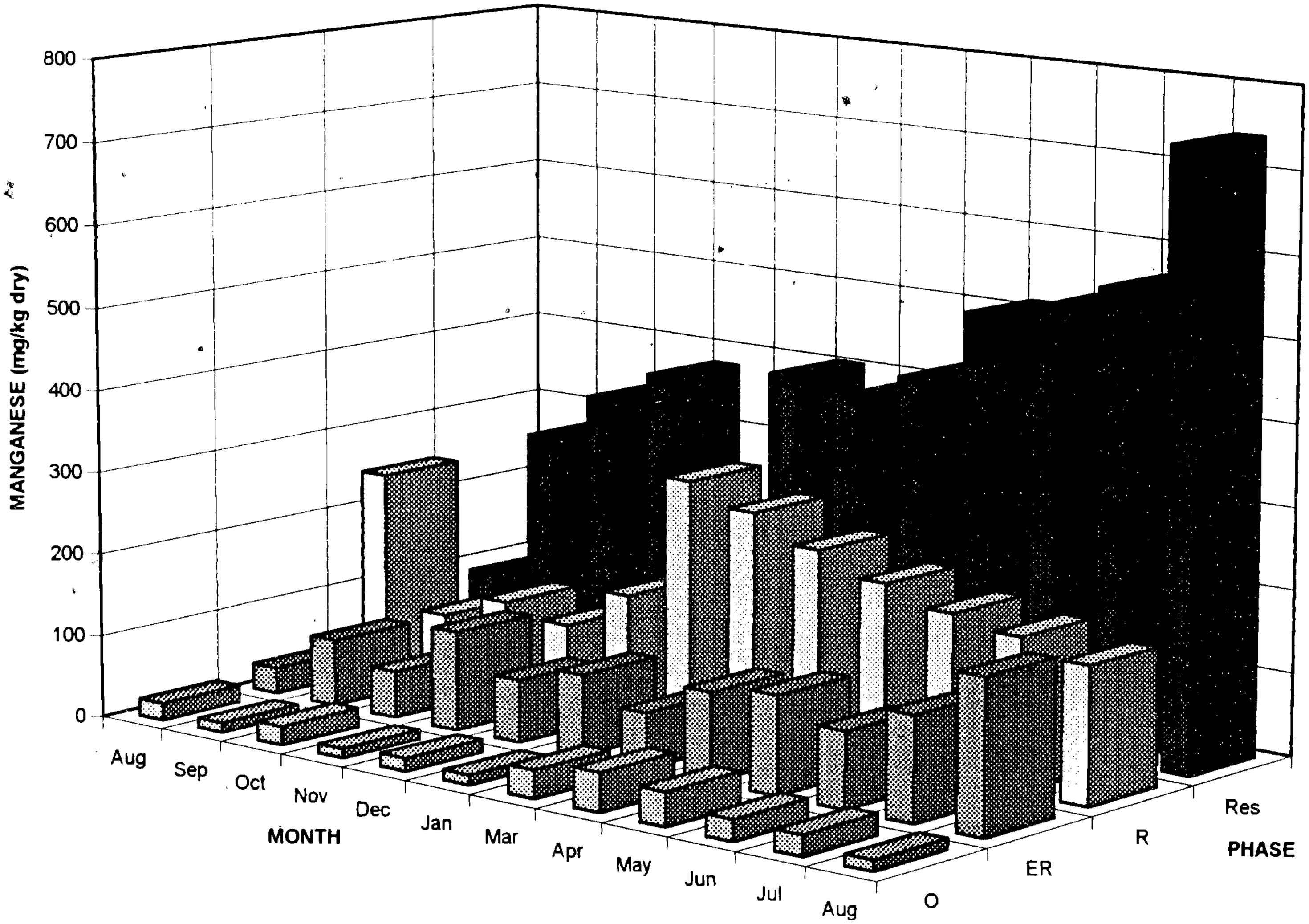


-EAD IN DEPOSITED SEDIMENT

LEAD IN SUSPENDED PARTICULATE MATTER



MANGANESE IN DEPOSITED SEDIMENT



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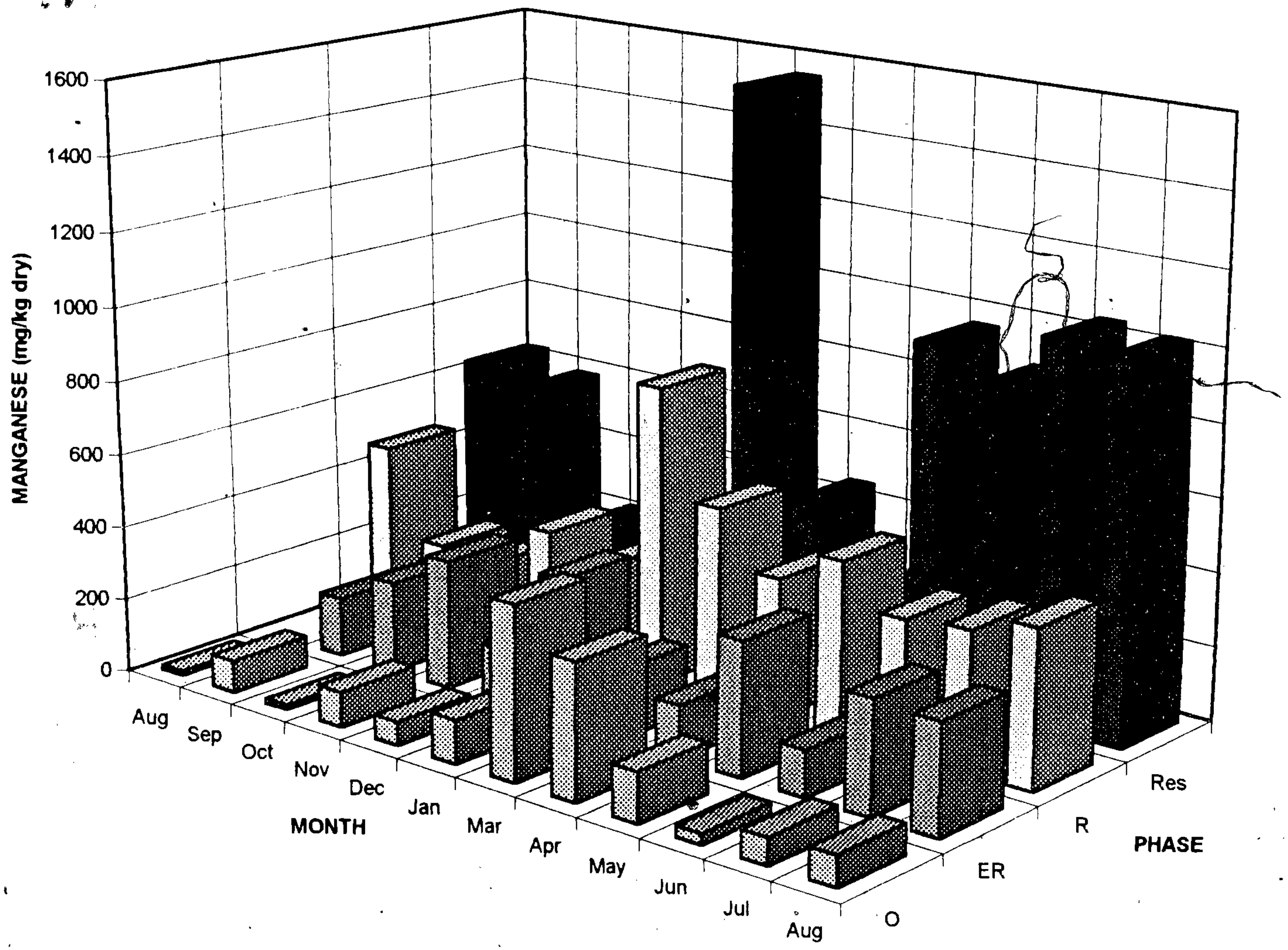

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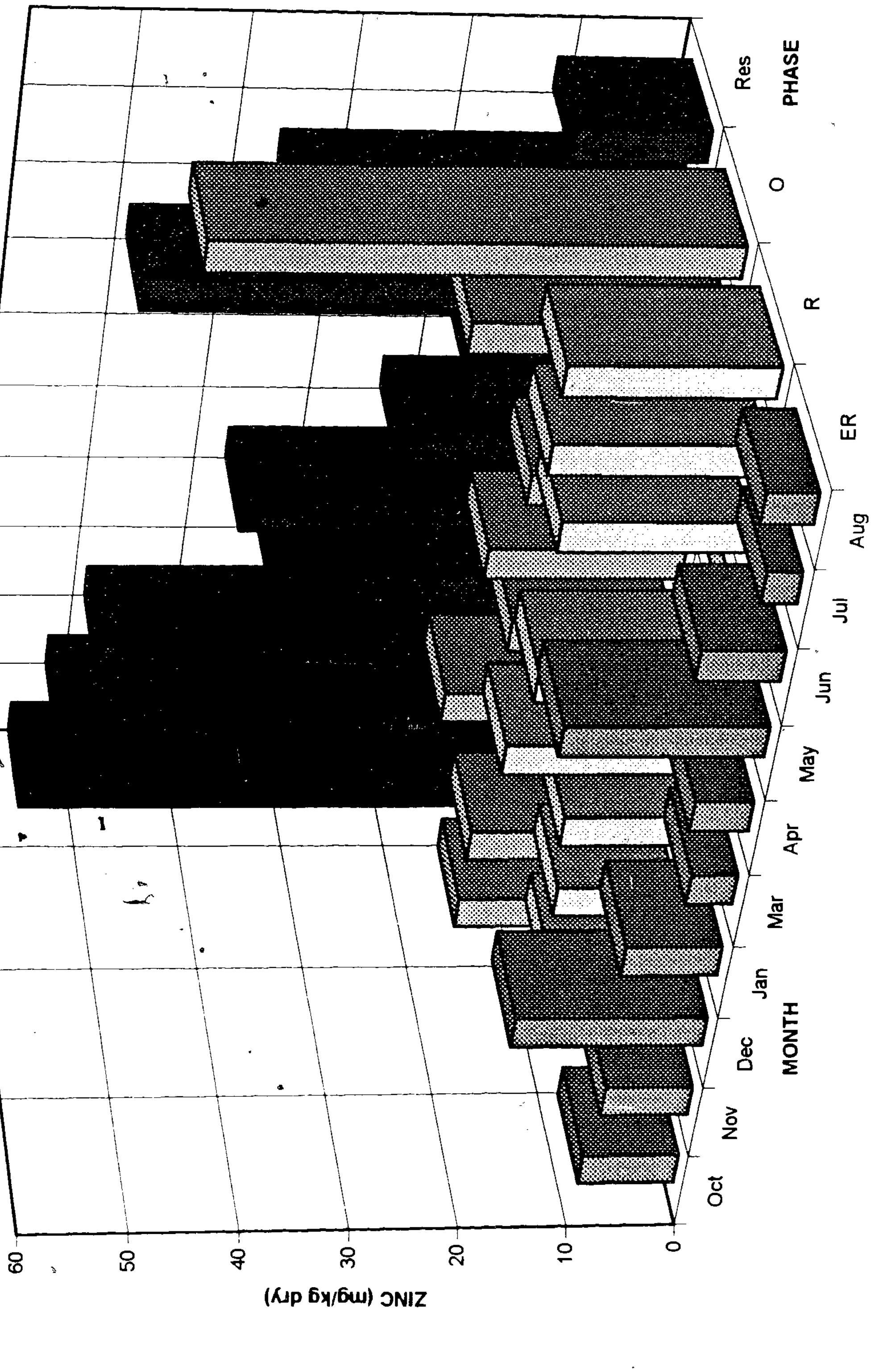

ZINC IN SUSPENDED PARTICULATE MATTER