GEOCHEMICAL BEHAVIOUR, FATE AND IMPACTS OF Cu, Cd AND Zn

FROM MINE EFFLUENT DISCHARGES IN HOWE SOUND

by

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ABSTRACT

The now abandoned mine at Britannia Beach is a source of acidity and heavy metals to Howe Sound. Using evidence from monthly field sample collections over an entire year, the dispersion patterns of Cu, Cd and Zn in the estuary were elucidated. Acid mine drainage discharged to Howe Sound via Britannia Creek was found to mix predominantly with the brackish surface waters, since a pronounced pycnocline inhibits vertical mixing. Deep discharges via a submarine outfall may become trapped at or below ten metres depth during summer, but have been observed to rise to the surface in winter as a result of weaker stratification.

Upon mixing with estuarine water, there was generally a transfer of Cu from the dissolved to the particulate phase. Similar removal was observed with Zn, albeit to a much lesser degree. Cd behaved essentially as a conservative element, which permitted its use as a tracer for the mixing of acid mine drainage with seawater. This greatly facilitated interpretation of the field data, since salinity proved to be an unreliable indicator of mixing in this three end-member system of Squamish River, Britannia Creek and seawater.

Laboratory mixing experiments demonstrated that the removal of Zn occurred via adsorption onto iron oxyhydroxides, with other processes such as adsorption by flocculated organic matter or by clays playing a less important role. Cu removal was additionally governed to a large extent by direct precipitation of solid phases, most likely $Cu(OH)_2$. Mixing experiments and speciation calculations suggest that Cu, and possibly Zn, may be present to a large degree in colloidal suspension.

Metal concentrations in estuarine surface waters ranged between 0.8 - 230, 0.02 - 2.9 and 1.7 - 450 μg/L for Cu, Cd and Zn, respectively at a site some 350 m off the mouth of Britannia Creek. They were found to be controlled by the supply from acid mine

drainage, by dilution with Squamish River runoff, and by the extent of removal in the creek mixing zone. All these parameters are strongly seasonal due to their dependence on hydrological conditions. They combined to produce maximum surface metal concentrations in spring and winter, as demonstrated using both field data and model calculations.

In a bioassay experiment, Cu concentrations over 6.4 μg/L affected growth of endemic phytoplankton adversely. This level was found to be exceeded in 13 out of 26 field observations in Britannia Bay. In spring, concentrations that could produce detrimental effects on phytoplankton may also extend several kilometres down-estuary.

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LIST OF ABBREVIATIONS

AMD	Acid mine drainage
ASV	Anodic stripping voltammetry
APDC	Ammonium pyrrolidine-dithiocarbamate
chl. a	Chlorophyll a
DDDC	Diethyl-dithiocarbamate
DDW	Distilled deionized water
DGT	Diffusive gel technique
diss.	Dissolved ($< 0.4\,\mu m$)
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
L	Litre
M	Mol/litre
MI	Mixing index
mL	Millilitre
mM	millimol/litre
mm	Millimeter
ng	Nanogram
part.	Particulate ($> 0.4\,\mu m$)
psi	Pounds per square inch (1 psi = 0.08 atm = 8014 Pa)
SEM	Scanning electron microscopy
SI	Saturation index
TPC	Total particulate carbon
μM	Micromol/litre
XRF	X-ray fluorescence (spectrometry)
w/w	Weight ratio

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Dedicated to those who care
about the Blue Planet
and who through their lives
try to make it the perfect place
it was intended to be.

CHAPTER 1

INTRODUCTION AND
BACKGROUND INFORMATION

1.1. Introduction

1.1.1. Motivation

Over its 70-year lifetime, the Britannia mine on the shore of Howe Sound extracted and processed some 40 million tons of ore, making it at times the largest copper producer in the British Commonwealth. In addition, the mining operation had a tremendous impact on the economic development of the Vancouver area earlier this century. Today, over twenty years after closure, the mine represents a significant environmental threat, since acid mine drainage (AMD) originating in the underground workings releases several hundred kilograms of copper and zinc daily to Howe Sound. At the same time, the site offers the opportunity to study in detail the chemical fate of a metal-rich acid solution as it is mixed with seawater.

The research presented in this thesis was fueled by these two related interests, the first representing an applied problem, and the second relating to questions of basic science. The application lies in investigating the dispersion and biogeochemistry of mine-derived metals in upper Howe Sound in order to complement earlier field and laboratory observations, which suggested that a variety of organisms suffered lethal or sublethal effects related to the high metal content of the local waters. Elevated metal concentrations could result from discharge of mine effluent and/or from release from submerged tailings. An extensive study on the geochemical behaviour of these deposits in Howe Sound indicated that they are not releasing significant amounts of Cu and Zn (Drysdale 1990). Consequently, the observed detrimental effects on marine organisms have been attributed to the discharge of mine effluent. However, the previous work did not define what areas of Howe Sound were affected by the discharge, how the acid solution behaved chemically in the estuary, and whether seasonal influences controlled its dispersion and behaviour.

Furthermore, as a point source of metals to a marine environment, the mine provided a basic scientific opportunity to study the transfer of metals between dissolved and particulate phases during the mixing of fresh- and saltwater. This is an important process in global metal cycles because it modifies the supply of riverborne terrigenous metals to the oceans. Additionally, since estuaries are often sites of intense industrial activity and human settlement, they are prone to contamination. The fate of anthropogenic metal inputs to the coastal ocean may be controlled to a large extent by dissolved/particulate partitioning of metals in estuaries.

1.1.2. Relevance and Objectives

Based on these initial considerations, five specific objectives related to the behaviour and effects of Cu, Cd and Zn from acid mine drainage in Howe Sound were defined, and are discussed in turn.

1) Water column data were needed to complement available information on mine effluent and sediment chemistry so as to provide a basis for decision making with respect to site treatment.

Earlier work has addressed metal chemistry in mine waters and in Britannia Creek (Steffen, Robertson, Kirsten 1991; Price et al. 1995) as well as metal release from sediments in Howe Sound that contain mine tailings (Drysdale 1990). However, there are almost no data on water column chemistry. Closing this gap is important, not only to assess the potential for environmental damage, but also to add to the sparse data available on the behaviour of mine effluents discharged directly to marine environments.

2) The dispersion and physico-chemical behaviour of the mine effluent in upper Howe Sound required assessing.

Dispersion patterns of mine effluent in Howe Sound have not been previously documented, even though they are a key factor in understanding the local impact of the metal-rich discharge. There is also very little information available on metal cycling in fjord-type estuaries in general, since most of the extensively studied estuaries are of the salt wedge or partially mixed type. There are many other industrial and mine sites that may release metals to a fjord, particularly in B.C. (e.g. mines on Vancouver Island), but also in other parts of the world (e.g. Norway, Chile, Greenland). The Britannia case may serve as an analogue for these sites, and the results presented here may have general applicability elsewhere.

The physico-chemical behaviour of metals is equally important when estimating the impacts of mine effluent in Howe Sound. This is particularly true for processes that remove metals from the water column, such as adsorption onto sinking particles. Should vertical transport of metals be significant, a sizable fraction could be permanently buried in the underlying sediments. Such processes could reduce dissolved metal concentrations and have beneficial effects for organisms living in the water column. The mechanisms by which metal removal occurs in contaminated environments are not well documented, and they may differ from the processes that have been described for more pristine estuaries. In addition, understanding these mechanisms is important for predictive models of metal pollution.

3) Seasonal influences on effluent chemistry and behaviour needed to be determined.

Parameters that may affect metal behaviour and concentration include pH, concentration of dissolved organic matter (DOC), suspended particulate load, riverine runoff, biological activity, creek runoff and AMD generation rates. All these parameters are likely to vary seasonally. Consequently, a seasonal study is needed to

determine natural variability in metal behaviour and concentration over the course of a year. There are very few studies in the literature which address this issue; in fact, most work on estuarine metal geochemistry is done in the summer months. Rather detailed studies include that by Sharp et al. (1982), who looked at Cu and Cd in the Chesapeake Bay during a spring phytoplankton bloom and during a period of high river runoff, work by Windom et al. (1991), who studied metal reactivity in the Medway estuary during periods of low and high river runoff, and a seasonal study of particulate matter in a Norwegian fjord by Skei and Melsom (1982). Flegal et al. (1991) compared data collected in April, August and December in the San Francisco Bay estuary. However, given the inherent high variability of estuaries with regard to their physical and chemical properties, higher sampling frequencies are needed both spatially and temporally in order to resolve seasonal differences.

4) Specific mechanisms involved in metal reactivity in the fresh-/saltwater mixing zone require elucidation.

In Howe Sound there is a localized region of mixing near the mouth of Britannia Creek, which in the following will be referred to as the "creek mixing zone". This mini-estuary within the estuary of Howe Sound is characterized by steep gradients in salinity, pH and metal concentrations over a distance of 100 - 200 m. Processes in the creek mixing zone such as adsorption, complexation or precipitation may determine the amount and physico-chemical form of metals delivered to Howe Sound. Additionally, since the mine effluent represents a point source of metals to Howe Sound, studying the processes in the creek mixing zone also provides an opportunity to learn more about metal cycling in estuaries in general.

5) The potential for detrimental effects on a natural population of phytoplankton needs to be determined.

Earlier laboratory studies on adverse effects of mine effluents on marine organisms in Howe Sound did not address the effects of the metal discharge on phytoplankton. This is an important subject because of the known sensitivity of phytoplankton to elevated trace metal concentrations and their position at the bottom of the food web. Reduction of the productivity of phytoplankton through discharges of AMD could affect the productivity of the entire ecosystem through reduction of the food supply to heterotrophic organisms (zooplankton, but also fish and shellfish). Accordingly, a bioassay experiment involving exposure of a natural assemblage of phytoplankton to AMD was designed and conducted.

1.1.3. Approach

The approach chosen to answer the questions discussed above included a large field component. In approximately monthly intervals over one year, samples were collected on a surface transect in the mixing zone of Britannia Creek and in two water column profiles in Britannia Bay (Figure 1.1). The data obtained (dissolved and particulate metal concentrations, pH, temperature, dissolved oxygen, salinity and chlorophyll a) were then complemented with specific experiments to address questions of particular interest, such as metal precipitation in the upper reaches of Britannia Creek, mechanisms of metal removal in the mixing zone, and speciation changes. In addition, a bioassay was conducted involving the exposure of a natural assemblage of phytoplankton to acid mine drainage. The results obtained using this approach will be presented in three separate chapters, and some background information pertaining to all of them will be given in the next section.

The map shows locations including Squamish River, Woodfibre, Watts Point, Brit. Creek, BRITANNIA MINE, Upper Sill, Porteau Cove, Gambier Island, Grace-Langdale Sill, Gibsons, Bowen Island, Horseshoe Bay, Strait of Georgia, and Vancouver. Points A and B are marked near Brit. Creek. A scale bar shows 0 to 10 km. A north arrow (N) is shown.

▨ Sites of vertical profiles
▨ Discrete surface samples
— Surface transect

Figure 1.1. Location of the Britannia mine and of the sampling sites in Howe Sound. The stations were occupied about once a month over a period of one year. The sites at Woodfibre and Porteau were visited only in September 1994. Also shown are the 100 and 200 m depth contours. Adapted from Thomson (1981).

1.2. Background Information

This section, intended for the benefit of the reader less familiar with certain aspects of this research, will sketch the setting and history of the study site, provide a summary on the generation of metal-rich effluents in mine settings, and dwell briefly on uses and biological importance of Cu, Cd and Zn. In addition, the physico-chemical properties of these elements and some aspects of their biogeochemistry will be highlighted.

1.2.1. Study Area and Mining History

Howe Sound is a 43 km long fjord in the vicinity of Vancouver, B.C. on the west Coast of Canada. Topographically it can be divided into two areas, the island-strewn lower basin, which is 20 km wide at its mouth and narrows into a 2 km wide channel, and the steep, narrow upper basin. The estuary is connected to the ocean via the Strait of Georgia. Its main source of freshwater is the Squamish River which enters at the northern end (Figure 1.1).

Although most of the east and west shores of Howe Sound have resisted settlement due to the steepness of the terrain and flood hazards on creek deltas, there are numerous sites where human activities could impact on the marine environment. Such activities include sewage discharges from communities in Squamish, Gibsons, Horseshoe Bay and Bowen Island. Others are the Port Mellon and Woodfibre pulp mills which used to be major sources of dioxins and furans to Howe Sound; however discharges of these compounds have greatly decreased in recent years as required by new provincial effluent guidelines. Industrial activity in the Squamish River delta has led to the loss of rearing habitat for young fish through construction, dyking of wetlands and log booming (Levings and Riedell 1992). There may also be metal inputs from industrial activity in

Squamish, although the discharge of acid mine drainage at Britannia Beach clearly represents the most important continuous source of metals to Howe Sound.

The Britannia mine was opened in 1902 by the Britannia Mining and Smelting Company, Ltd. In 1963, it was taken over by the Anaconda Mining Company, who operated it until the ore body was exhausted in 1974. It was then bought by Copper Beach Estates Ltd. for real estate development. At the time of writing, the company is under receivership, and the future uses of the property are uncertain.

The Britannia ore body is a volcanogenic massive sulphide deposit located in a steep mountain ridge rising to over 1000 m above sea level. Mining was carried out mostly underground, but several surface pits were also excavated at higher elevations. During operation, the ore was transported to the Britannia Beach townsite for milling and was then smeltered off-site. Over the lifetime of the mine, almost 49 million tonnes of ore were processed, producing 517,000 tonnes of copper, 125,000 tonnes of zinc, 16,000 tonnes of lead, 444 tonnes of cadmium, 180 tonnes of silver and 15 tonnes of gold (Price et al. 1995).

Large amounts of mine tailings were landfilled on site or discharged as a slurry to Howe Sound. Copper concentrations in sediments off Britannia Beach have been found to be as high as 1400 ppm, over 17 times higher than levels found in other parts of the inlet (Thompson and Paton 1976). After discharge of tailings ceased with closure of the mine, new uncontaminated sediment has been accumulating at a rate of about 1 cm/year, thereby effectively burying and immobilizing the tailings (Drysdale 1990). However, there remains the potential for slumping of tailings deposited on the steep flanks of the basin.

Over 80 km of shafts and adits were driven into the deposit to access the ore. This generated a large surface area of residual ore exposed to weathering by air and infiltrating water. Rain- and groundwater enter the mine mostly via the open pits and carry the oxidation products - acidity and dissolved metals - out of the mine through two adits at

about 700 and 67 m above sea level (the so-called 2200 and 4100 portals, respectively). Under a provincial permit, this acid mine drainage from the 2200 portal is allowed to mix with Britannia Creek which then flows to Howe Sound, while the 4100 discharge is routed directly to the estuary via a 30 m deep outfall (Price et al. 1995).

1.2.1. Acid Mine Drainage

The naturally occurring oxidation of sulphide minerals, particularly pyrite, is a common process in mining operations where it is referred to as acid mine drainage (AMD). It is an environmental concern due to the acidity produced and the release of heavy metals associated with the ores.

The dissolution and oxidation of pyrite involves a series of reactions as follows (Stumm and Morgan 1996):

$$FeS_2(s) + 7/2 O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1.1}$$

$$Fe^{2+} + 1/2 O_2 + H^+ \rightarrow Fe^{3+} + 1/2 H_2O \tag{1.2}$$

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{1.3}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \tag{1.4}$$
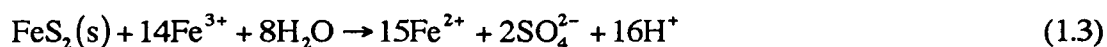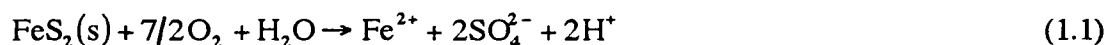
Pyrite is oxidatively dissolved as it is exposed to oxygen and water (1.1). Subsequently, the dissolved ferrous iron undergoes oxidation to ferric iron (1.2), a redox reaction with O_2 acting as electron acceptor. Ferric iron may then be used in the further oxidative dissolution of pyrite by reaction (1.3). This step is analogous to reaction (1.1) with ferric iron acting as an oxidant instead of molecular oxygen. Ferric iron can also form insoluble precipitates (1.4).

The oxidation of ferrous iron to ferric iron (1.2) is slow and determines the overall reaction rate. The ferric iron produced in (1.2) is rapidly consumed by the further oxidation of pyrite (1.3) or by the precipitation as iron hydroxide (1.4), giving rise to the insoluble $Fe(OH)_3$ deposits ("yellow boy") commonly associated with mine waters.

In natural systems, strains of acid-tolerant bacteria such as *Thiobacillus ferrooxidans* increase the rate of ferric iron oxidation (1.2) catalytically by up to a million-fold compared to abiotic systems (Nordstrom 1985), thereby increasing the overall reaction rate of pyrite oxidation. Taylor et al. (1984), for example, observed a two to five-fold higher sulphate production rate with pyrite inoculated with *Thiobacillus ferrooxidans* relative to the sterile control experiment. The discrepancy between the acceleration of ferrous iron oxidation and the comparatively small increase in sulphate production rates may stem from poor growing conditions in the experiment of Taylor et al. (1984), but it could also indicate that bacterial mediation is not as important as is often assumed.

Acid producing reactions in mining environments can pose environmental problems for several reasons. The generation of acidity is a major concern, since for every mole of pyrite converted to $Fe(OH)_3$, four moles protons are released into the environment, making this one the most acid-generating weathering reaction. In addition, metals associated with the pyritic ore, e.g. Zn and Cu, are released from their rock matrix and are delivered to the environment in concentrations that may be harmful to organisms. Further, it is almost impossible to stop the oxidation process, since exposure of the deposit to molecular oxygen would need to be prevented. In fact, cessation of mining activities often aggravates the problem of acid mine drainage, since the water is no longer drained regularly and exposure time for acid-producing reactions is increased. Furthermore, generation of AMD will persist for as long as there are sulphidic ores in the mine that are exposed to water, which often means that the processes will continue for decades or even centuries. Therefore, effective measures to cope with AMD and to

prevent damage to the environment have to be an integral part of any mining operation and must be included in the cost of extraction of metals from ores for human use.

1.2.3. Human Uses , Biological Importance and Physical-Chemical Properties of Cu, Cd and Zn

Although Cu, Cd and Zn are considered trace metals due to their low abundance in the earth's crust (Cu: 50 ppm, Zn: 70 ppm, Cd: 0.15 ppm, Krauskopf and Bird 1995), they can be readily obtained from ores, or, as in the case of Cu, they may also be found in metallic form. Copper is widely distributed in nature in sulphides, arsenides, chlorides and carbonates and as the pure metal. Zn is present mostly as sphalerite ((ZnFe)S). Cd minerals are rare, but the element can often be found as an isomorphous substitute for Zn in ores. Of the three metals, Cu is produced in the largest amounts (World Bureau of Metal Statistics 1993).

Copper has wide industrial use owing to its capability of forming alloys to give new materials with unique properties. Other uses include electrical applications (wires, generators), construction (plumbing) and chemical manufacturing (catalysts, fungicides) (Bowen and Gunatilaka 1977). A major fraction of the annual Zn production is consumed for galvanizing steels and for forming alloys. It is also widely used for battery casings, as pigment, and for cosmetic products (Mathewson, 1970). About 75% of the total Cd produced goes into the manufacturing of corrosion-resistant steels. Other important applications include batteries and pigments (Webb 1979).

Cu plays an important role in biological systems as an electron acceptor/donor. The Cu^+/Cu^{2+} pair is found for example in plastocyanin and in photosystem II of higher plants. In the oceans, Cu has been shown to be a required micronutrient for phytoplankton, but to be toxic at higher concentrations (e.g. Sunda 1994). Zinc is known

to occur in virtually all organisms, mainly as a cofactor in enzymes involved in the lipid, carbohydrate and protein metabolisms. Like Cu, Zn has a function as both nutrient and toxic agent to marine phytoplankton (Sunda 1994). Despite its chemical similarity to Zn, Cd is not thought to have an essential role in biological systems. In the oceans it appears to behave as a micronutrient, although its metabolic function is unclear. In some enzymes Cd may replace Zn under conditions of Zn limitation (Price and Morel 1990).

	Cu	Zn	Cd
Outer Electron Configuration	$[Ar]3d^{10}4s^1$	$[Ar]3d^{10}4s^2$	$[Kr]4d^{10}5s^2$
Atomic Weight	63.546	65.39	112.41
Ionization Potential [eV] 1.	7.72	9.39	8.99
2.	20.29	17.89	16.84
3.	39.7	40.0	38.0
Melting Point [°C]	1084	419	321
Boiling Point [°C]	2595	907	767

Table 1.1. Some physical properties of the elements Cu, Cd and Zn. Adapted from Cotton-Wilkinson (1972) and Heslop and Jones (1976).

Cu, Cd and Zn share some properties common to transition elements, namely their metallic character, the stability of the ionic form, the capability of forming complexes with both organic and inorganic ligands, and their relatively low ionization potentials. However, Cu is set apart from Cd and Zn both with respect to physical properties (Table 1.1) and chemical reactivity as a result of its different outer shell electron configuration. With Cu stable +I complexes are common, while Cd and Zn are present almost exclusively in the +II oxidation state. Cu^+ is readily oxidized to Cu^{2+}, which is the basis for its importance in biological electron transfer reactions. All three metals form complexes with inorganic ligands such as CO_3^{2-}, Cl^- or OH^-. According to the Pearson concept, Cu is the hardest acid of the three, thus likely to complex with O and N-donors,

while Cd as a soft acid complexes more readily with S and P-donors. Metal-organic complexes are most common with Cu, but are also found with Zn and Cd. All three metals form halide, oxide and sulphide salts, the latter being quite insoluble (Cotton and Wilkinson 1972). The physico-chemical properties particular to each metal have a bearing on the global biogeochemical cycling of Cu, Cd and Zn, and as will be shown later, also greatly influence their behaviour upon mixing with seawater in Howe Sound.

1.2.4. Biogeochemical Cycling of Cu, Cd and Zn

Over the last two decades, a consistent picture of the biogeochemistry of trace metals has emerged. This was made possible to a large part by the use of trace metal clean sampling protocols and the advent of new, more sensitive analytical techniques, which enabled researchers to determine accurately the very low concentrations of metals in the oceans (Bruland et al. 1991). Some representative concentrations of Cu, Cd and Zn are given in Table 1.2.

	Cu [μg/L]	Cd [ng/L]	Zn [μg/L]
U.S. East Coast Rivers	1.1	11	0.84
Lake Constance, Switzerland	0.3 - 1.3	5.6 - 28	0.98 - 3.9
North Pacific	0.03 - 0.3	1.1 - 11	0.006 - 0.65

Table 1.2. Representative concentrations of Cu, Cd and Zn in natural waters (from Stumm and Morgan 1996).

Physical and chemical weathering of rocks on land provides the ultimate source of metals to the oceans. Themetals are transported to the oceans via in dissolved or particulate form by streams and rivers or as dust by the wind. Riverine inputs exceed those from the atmosphere (Table 1.3) and comprise a large proportion of weathering

products mostly in the form of particles (Emeis 1985). Atmospheric sources include volcanic emissions, windborne soil particles, forest fires and human activities such as burning of fossil fuels and metal smelting and refining. Metals are removed from the ocean primarily via sinking particles, either through biological mechanisms (uptake by bacteria, phytoplankton and higher organisms with subsequent transport to the sediments via sinking organic debris) or through physico-chemical processes (adsorption onto particles, particle aggregation, precipitation). Other sinks include sediment pore waters, ferromanganese crusts and salt spray deposition. The cycle closes as sedimentary rocks are uplift through tectonic forces and become subject to weathering.

Fluxes in 10^3 tonnes/year		Cu	Cd	Zn
SOURCES	Continental dust	10	0.25	25
	Volcanic dust	9.3	0.04	11
	Industrial part. emissions	220	4	700
	Fossil fuels	43	1.5	140
PATHWAYS	Atmospheric rainout	260	51	1000
	Stream load	1100	120	2500
HUMAN USE	Production of refined metal	10800	20	2990

Table 1.3. Sources and pathways of metal fluxes to the oceans. For comparison, the amount of refined metal produced annually is also shown. Note that sources include only atmospheric contributions. From Lantzy and Mackenzie (1979) and the World Bureau of Metal Statistics (1993).

Metals show great differences in their chemical reactivity during the part of the cycle they spend in the hydrosphere. This is reflected in their residence time in the oceans, commonly defined as:

$$\tau_{in} = \text{(inventory in oceans) / (rate of input from all sources)} \qquad (1.5)$$

$$\tau_{out} = \text{(inventory in oceans) / (rate of removal by all sinks)} \qquad (1.6)$$

Elements with long residence times (e.g. Na 8.3×10^7 years, Cl $> 10^{10}$ years, Broecker and Peng 1982) are essentially non-reactive, their main sinks being interstitial sediments and evaporites. The involvement of Cu, Cd and Zn in biological uptake and vertical particle transport results in residence times on the order of $10^3 - 10^5$ years (Cu: 1000 - 6400 years, Boyle et al. (1977), Bewers and Yeats (1977); Cd: 7700 - 45,000 years, Bewers and Yeats (1977), Bruland et al. (1994); Zn: 3000 - 92,000 years, Bewers and Yeats (1977), Shiller and Boyle (1984), Bruland et al. (1994)) The tendency of Fe to form insoluble hydroxides leads to much shorter residence times of less than 100 years (Broecker and Peng 1982, Bruland et al. 1994, Bewers and Yeats 1977).

Reported residence time estimates may vary over several orders of magnitude, depending on the reservoir (e.g. deep ocean, coastal ocean) and mechanism (e.g. riverine input, scavenging by particles) considered. In recent years, estimates obtained by different methods have been converging. This may in part be the result of improved analytical procedures. For example, Shiller and Boyle (1985) showed that some earlier residence time calculations were based on overestimates of riverine Zn fluxes, which have resulted from inadequate contamination control during collection and analysis of river water samples. Using their revised flux estimates, they calculated a residence time for Zn of about 50,000 years, two orders of magnitude longer than previous estimates.

Thanks to the techniques now available, the oceanic metal inventory is quite well constrained. With regard to input-based residence times, estimating the magnitudes of the sources is more difficult, since they often exhibit considerable spatial and temporal variability. River flows can change tremendously over the course of a year, and metal concentrations in rivers are highly dependent on area, season, and human activity. In addition, the riverine metal load can be altered significantly by estuarine removal or release processes. Studies investigating such processes both in the world's major rivers as well as in contaminated streams are essential for obtaining good residence time estimates and for fostering our understanding of the biogeochemical cycling of metals in general.

1.3. Organization

The results and findings of this study will be presented in the following three chapters. In Chapter 2, a one-year set of monthly field data is used to deduce dispersion patterns of acid mine drainage in Howe Sound and their dependence on seasonal influences. Chapter 3 contains an investigation into the physico-chemical reactions leading to the observed behaviour of metals in the creek mixing zone. The results of a bioassay involving exposure of a natural assemblage of phytoplankton to elevated concentrations of metals from AMD are discussed in Chapter 4. Finally, conclusions from the entire thesis and recommendations for future research are given. The three main chapters are written as stand-alone sections, thereby facilitating publication as scientific papers. However, they are linked by a global introduction (Chapter 1) and discussion (Chapter 5) as well as by their inherent close connection. This format may lead to some minor redundancies, but care was given to avoid these as much as possible. It was felt that disadvantages arising from choosing this format were outweighed by the relative ease and speed of publication of the results.

1.4. References

Bewers, J.M. and P.A. Yeats, 1977. Oceanic residence times of trace metals. Nature **268**, 595 - 598.

Boyle, E.A., R.F. Sclater and J.M. Edmond, 1977. The distribution of dissolved copper in the Pacific. Earth Planet. Sci. Lett. **37**, 38 - 54.

Bowen, R. and A. Gunatilaka, 1977. Copper: its geology amd economics. Applied Science Publishers, London.

Broecker, W. and T.-H. Peng, 1982. Tracers in the Sea. Lamont-Doherty Geological Observatory, Palisades, NY.

Bruland, K.W., J.R. Donat and D.A. Hutchins, 1991. Interactive influence of bioactive trace metals on biological production in oceanic waters. Limnol. Oceanogr. **36**, 1555 - 1577.

Bruland, K.W., K.J. Orians and J.P. Cowen, 1994. Reactive trace metals in the stratified North Pacific. Geochim. Cosmochim. Acta **58**, 3171 - 3182.

Cotton, F.A. and G. Wilkinson, 1972. Advanced Inorganic Chemistry. Wiley, New York.

Drysdale, K., 1990. Geochemistry of buried marine mine tailings deposit, Howe Sound, BC. M.Sc. thesis, University of British Columbia, Vancouver.

Emeis, K., 1985. Particulate suspended matter in world rivers - II: results on the rivers Indus, Waikato, Nile, St. Lawrence, Yangtse, Parana, Orinoco, Caroni and Mackenzie. SCOPE/UNEP Sonderband Heft **58**, 593 - 617.

Flegal, A.R., G.J. Smith, G.A. Gill and S. Sanudo-Wilhelmy, 1991. Dissolved trace element cycles in the San Francisco Bay estuary. Mar. Chem. **36**, 329 - 363.

Heslop, R.B. and K. Jones, 1976. Inorganic Chemistry. Elsevier, Amsterdam.

Krauskopf, K.B. and D.K. Bird, 1995. Introduction to Geochemistry. 3rd ed., McGraw-Hill, New York.

Lantzy, R.J. and F.T. Mackenzie, 1979. Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta **43**, 511 - 525.

Levings, C.D. and B.E. Riddell, 1992. Salmonids and their habitats in Howe Sound Basin: status of knowledge. Proceedings of the Howe Sound Environmental workshop, 1992. Can. Tech. Rep. Fish. Aquat. Sci. **1879**, 66 - 74.

Mathewson, C.H., 1959. Zinc: the science and technology of the metal, its alloys and compounds. American Zinc Institute ed., Reinhold, New York.

Nordstrom, D.K., 1985. The rate of ferrous iron oxidation in a stream receiving acid mine effluent. USGS Water Supply Paper 2270, 113 - 119.

Price, N.M. and F.M.M. Morel, 1990. Cadmium and cobalt substitution for zinc in a marine diatom. Nature **344**, 658 - 660.

Price, W.A., T. Schwab and N. Hutt, 1995. A reconnaissance study of acid mine drainage at the Britannia mine. B.C. Ministry of Energy, Mines and Petroleum Resources, Victoria, B.C.

Sharp, J.H., C.H. Culberson and T.M. Church, 1982. The chemistry of the Delaware estuary: general considerations. Limnol. Oceanogr. **27**, 1015 - 1028.

Shiller, A.M. and E. A. Boyle, 1985. Dissolved zinc in rivers. Nature **317**, 49 - 52.

Skei, J.M. and S. Melsom, 1982. Seasonal and vertical variations in the chemical composition of suspended particulate matter in an oxygen-deficient fjord. Estuar. Coastal Shelf Sci. **14**, 61 - 78.

Steffen, Robertson and Kirsten, 1991. Evaluation of ARD from Britannia Mine and the options for long term remediation of the impact on Howe Sound. Steffen, Robertson and Kirsten (B.C.) Inc., Vancouver.

Stumm, W.S. and J.J. Morgan, 1996. Aquatic Chemistry, 3rd ed., Wiley, New York.

Sunda, W.G., 1994. Trace metal/phytoplankton interactions in the sea. In: Chemistry of aquatic systems: Local and global perspectives, G. Bidoglio and W. Stumm eds., ECSC, EEC, EAEC, Brussels and Luxembourg, 213 - 247.

Taylor, B.E., M.C. Wheeler and D.K. Nordstrom, 1984. Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. Geochim. Cosmochim Acta **48**, 2669 - 2678.

Thompson, J.A.J. and D.W. Paton, 1976. Further studies of mine tailings distribution in Howe Sound, B.C. Fish. Res. Bd. Can. Man. Rep., 1383, Fisheries Research Board of Canada, Nanaimo, B.C.

Thomson, R.E., 1981. Oceanography of the British Columbia coast. Canadian Special Publication of Fisheries and Aquatic Sciences 56. Department of Fisheries and Oceans, Ottawa.

Webb, M., 1979. Chemistry, Biochemistry and Biology of Cadmium. Elsevier, Amsterdam, 74.

Windom, H., J. Byrd, J. R Smith, M. Hungspreugs, S. Dharmvanij, W. Thumtrakul and P. Yeats, 1991. Trace metal-nutrient relationships in estuaries. Mar. Chem. **32**, 177 - 194.

World Bureau of Metal Statistics, 1993. World metal statistics yearbook 1992, London.

CHAPTER 2

METAL DISPERSION IN HOWE SOUND: MECHANISMS AND SEASONALITY

2.1. Introduction

Concerns about metal concentrations in Howe Sound waters reaching levels potentially toxic to marine organisms, and the lack of data to address these concerns, prompted a detailed investigation into the mechanisms of metal dispersion and the fate of acid mine drainage. Specific areas of interest included questions such as: can a general pattern of metal dispersion in the estuary be identified and what area is affected by the mine discharge? How does dispersion change with seasonally variable parameters such as river runoff, AMD discharge and biological activity? During what time of the year are toxic effects on biota most likely? Is there any benefit in discharging metal at depth rather than at the surface?

Three main pieces of information are needed to provide keys to these questions. Metal sources and their seasonal variability have to be identified, the physico-chemical behaviour of metals upon discharge to the marine environment needs to be investigated, and the transport mechanisms of metals in the estuary have to be known. With this information at hand, a simple model of metal dispersion may be established which can both serve to improve our conceptual understanding of metal dispersion and to make predictions based on a few key variables.

There are two point sources of acid mine drainage to upper Howe Sound, namely Britannia Creek and a submarine outfall off the beach at the Britannia town site. Records from various sources compiled by Price et al. (1995) indicate that both the concentrations of metals in these sources and metal loadings (concentration times discharge) are subject to substantial seasonal variability. Metal loading from acid mine drainage may peak after periods of heavy rainfall (Walling and Foster 1975, Johnson and Thornton 1987, Robertson 1990). Because substantial metal discharges could harm marine life in Howe Sound, it is important to identify times when metal loadings are most likely to be high.

The amount of metal delivered will also depend on whether removal or release processes occur during mixing of acid mine drainage with salt water, and on the extent of such reactions. Metals can be removed from solution during estuarine mixing by precipitation as insoluble phases, by adsorption onto settling particulate matter, via complexation by organic surface coatings of particles, or by flocculation and aggregation of colloid-sized particles (Stumm et al. 1994, Duinker 1980). Removal of Cu, Cd and Zn have all been observed under some circumstances (e.g. Windom et al. 1991, Duinker 1983). Alternatively, metals can be released into solution by ion exchange on particle surfaces or by complexation of adsorbed metals by dissolved ligands (Li et al. 1984, Duinker 1980). Observed mid-salinity maxima of dissolved Cu, Cd and Zn have been attributed to such processes (Flegal et al. 1991, Salomons and Förstner 1984). Additionally, metals can pass the mixing zone without being affected by release or removal processes. This so-called conservative behaviour is documented for Cu and Cd in Sharp et al. (1982) and Windom et al. (1991). Obviously, the occurrence and extent of such processes is dependent on the local conditions and can not be easily predicted. Identifying the extent of removal or release of metals from acid mine drainage in the mixing zone and the dependence of these processes on seasonal parameters is essential for estimating the effective metal load delivered to Howe Sound.

Much of the information needed to address the issue of metal dispersion is closely linked to the physical properties of the system (estuarine circulation and hydrology), and it is important to have information on different types of estuaries in order to understand how physical characteristics influence the fate of anthropogenic metal contamination. Generally, dissolved metal concentrations in surface waters will decrease towards the mouth of an estuary due to increasing dilution of the metal source with more saline water. At the same time, there may also be lateral and vertical gradients. While the longitudinal ones are adequately discussed in the literature, the lateral and vertical gradients in metal concentrations are not well documented. Vertical gradients have been described in the

Fraser, St. Lawrence and Puget Sound estuaries. In the Fraser River estuary, dissolved Fe, Cu and Cd profiles reflect the movement of the salt wedge and are influenced by the rate of mixing and the salinity contrast of the end-members (Fletcher et al. 1983). In the St. Lawrence, total metal concentrations increased in the vicinity of the turbidity maximum (Bewers and Yeats 1979). In Puget Sound, high Cu and Zn concentrations from urban sources are propagated from the surface to deeper waters via advection and particle transport (Paulson et al. 1988). In Hood Canal, a fjord-type branch of Puget Sound, almost uniform metal concentrations with depth were interpreted to reflect the combined effect of small inputs (the area is sparsely populated), biological uptake at the surface and regeneration at depth (Paulson et al. 1993). Generally, in fjord-type and stratified estuaries lateral gradients are not commonly documented, and metal profiles are sparse. Apparently, lateral and, below the pycnocline, vertical homogeneity is assumed. Clearly, this assumption is not valid in Howe Sound, where metal inputs occur both laterally and at depth, and it may also not hold true in other estuaries.

The pioneering work of Morton (1959) on the behaviour of density-driven plumes has shown that upon discharge of freshwater at depth, its density increases as the water rises and mixes with the surrounding salt water. Depending on the density gradient and the discharge volume, the discharge may either rise all the way to the surface or reach a state of neutral buoyancy at some depth. The latter effect often occurs when a strong pycnocline is present and has been observed in numerous cases, such as in a submarine Arctic freshwater spring (Colbourne and Hay 1990), in industrial effluent in a fjord (Skei et al. 1973), and in municipal sewage discharged to coastal waters (Scanes and Philip 1995). Depending on the density structure of the water column, acid mine drainage discharged at depth in Howe Sound may be trapped below the pycnocline or contribute to the surface metal load.

In well-stratified estuaries, box models have been used successfully to describe the circulation-driven dispersion of metals and nutrients (Bewers and Yeats 1978, Petrie and

Yeats 1990, Shiller 1996). A simple box model that makes use of evidence from a one year set of monthly vertical profiles and from corresponding creek metal concentrations (corrected for losses due to removal processes) is used here to shed some light on metal dispersion in upper Howe Sound.

2.2. Materials and Methods

2.2.1. Field Program

Approximately monthly sampling surveys were carried out over the course of a year at a suite of established sites. Sampling was conducted from the UBC Oceanography workboat. Surface water and particulate samples were collected at approximately 10 sites. In addition, samples were collected at depths of 0, 5, 10, 30, 50 and 80 m at a site close to the mine ("Station B", see also Figure 1.1, Chapter 1) and at 0, 5, 10, 30, 50, 80 and 200 m at an offshore site ("Station A") to evaluate the vertical distribution distribution of Cu, Cd, Zn and Fe.. Subsamples were taken for pH, dissolved oxygen, chlorophyll $\underline{a}$ and in some cases dissolved organic carbon (DOC) measurements. An S4 current meter was used to complement the trace metal data with temperature and salinity profiles. Surface, 5 and 10 m samples were collected by means of a peristaltic pump with acid-cleaned Tygon tubing, while the deeper samples were obtained using a 10 L GOFlo sampling bottle (General Oceanics Inc., Miami, FL) attached to a Kevlar line. Samples were drawn into acid-cleaned 250 mL low density polyethylene bottles, bagged and stored on ice for transport to the lab. All further manipulations were performed in a class 100 clean room.

Between December 2, 1993 and January 13, 1994, sediment traps were deployed at Station A (30, 50 and 200 m below surface) and Station B (30, 50, 80 m). Traps were hung in pairs, with one containing formaldehyde as a preservative. The traps, 50 cm long PVC-tubes with a diameter of 12.5 cm, had a baffle at the top and in the collection cup to prevent resuspension of particulate matter. They were washed with detergent, distilled water and dilute HCl, and the collection cup was filled with NaCl brine (20% w/w) before deployment. Upon retrieval, the water above the collection cups was siphoned off, and the traps were brought back upright to the laboratory.

An automatic sampler (ISCO 2900, ISCO Inc., Lincoln, NE) was installed at the 4100

portal to collect sequential samples (one every two days over a period of one year) for the

monitoring of the metal content of the discharge. The samples were recovered in roughly

monthly intervals, brought to the lab, analyzed for pH and then acidified with nitric acid

to pH < 2. Total Cu, Cd, Zn and Fe in unfiltered, acidified samples were measured by

GFAAS. Weekly flow records at the 4100 portal for January through April 1994 were

provided by Copper Beach Estates Ltd. and for August 1995 through January 1996 by the

B.C. Ministry of Environment.

2.2.2. Analytical Program

Water samples were filtered within eight hours of collection through 0.4 μm acid-

cleaned polycarbonate membranes and acidified to pH < 2 with 500 μL environmental

grade HNO_3. Degradation of residual organic matter in the dissolved fraction was

enhanced by keeping the samples at 65°C for two weeks prior to analysis as suggested by

Paulson (1986). The filters containing the particulate fraction were folded, placed into

polyethylene vials and dried in a convection oven. Dissolved metals (Cu, Cd, Zn, Fe)

were determined by graphite furnace atomic absorption spectrometry (GFAAS) after

organic extraction; particulate metals were microwave digested and analyzed by

inductively coupled plasma mass spectrometry (ICP-MS).

Chlorophyll a was determined using a method similar to Parsons et al. (1989) by

filtering 100 mL seawater through precombusted glass fiber filters (Whatman GF/F) in

the field. The filters were kept on ice, brought to the lab, removed from the filter holders

and frozen. Within six months, the samples were thawed and sonicated with 90%

acetone. The amount of chlorophyll a per mL seawater was determined by fluorescence

(Turner 10 AU fluorometer, Turner Industries, Sunnyvale, CA) .

DOC samples were filtered through combusted (550°C, 4 hours) glass-fibre filters (Whatman GF/F) into combusted Pyrex bottles. 500 μL of 0.125 M HgCl$_2$ solution (ACS grade, Fisher Scientific Co., Fair Lawn, NJ) was added to each 250 mL sample to prevent losses by bacterial degradation. The samples were stored frozen until analysis. Measurements were performed on acidified (10% H3PO4, 1:20) degassed samples by the high temperature catalytic oxidation method (HTCO, Suzuki et al. 1992) at the Institute of Ocean Sciences, Sidney (B.C.). Instrumentation used consisted of a Sumigraph TOC-90 carbon analyzer (Sumika Chemical Analysis Service Ltd., Osaka) and a Rosemount Model 800 non-dispersive infrared analyzer (Rosemount Analytical Inc., La Habra CA) interfaced with a Shimadzu C-R4A Chromatopac chromatocorder (Shimadzu Corp., Kyoto). Standards were prepared from potassium hydrogen phtalate (AnalaR, BDH Chemicals Ltd., Poole, G.B.) in fresh DDW. Instrumental blanks were determined by running fresh DDW samples.

Dissolved oxygen was determined by the Winkler method (Parsons et al., 1989) or by using a field probe equipped with oxygen, pH, temperature and conductivity sensors. Coherence of the two methods was achieved by performing both measurements on several sets of samples and applying the corresponding calibration curves to those datasets that were obtained using the probe only.

Salinity, temperature and pH were measured using the same combination probe, or alternatively with an S4 current meter for salinity and temperature and a Ross pH-electrode (Orion Research Inc., Boston, MA). In this case, pH determinations were performed in the laboratory. Again the different measuring devices were intercalibrated to achieve consistent results. The field probe did not always work satisfactorily. Values considered to be erroneous are marked with brackets in Appendix A.2 and were not used for data interpretation.

Particulate material collected in sediment traps was passed through 0.5 mm mesh to remove larger heterotrophs, centrifuged and freeze dried. Prior to analysis, samples were

ground in an agate mortar. For minor elements (Cu, Zn), 1 g of sample was pressed into a pellet backed by boric acid using the method of Calvert et al. (1985), adapted for small samples. Fused-glass discs were prepared for major elements (Al, Fe), again after Calvert et al. (1985). Metals were analyzed by X-ray fluorescence analysis on a Philips model PW 2400 spectrometer (Philips Electronics N.V., Eindhoven, Netherlands). The instrument was calibrated against marine sediment reference standards. Values reported are not corrected for salt or for losses that might have occurred due to desorption of metals from collected particles (Knauer et al. 1984).

2.2.3. Determination of Dissolved Metals

Preconcentration and removal of interfering sea salt was achieved by organic extraction using 1-pyrrolidinedithiocarbamate / sodium diethyldithiocarbamate (APDC/DDDC) and back-extraction into nitric acid. The method was modified from the one described by Bruland and Coale (1985). Briefly, about 50 g of sample was adjusted to pH 4 - 4.5 by adding 1 mL of concentrated NH_4OAc (pH 6) and extracted into 20 mL chloroform with 250 μL APDC/DDDC-solution by shaking for 3 min. on a mechanical shaker. After phase separation the organic fraction was transferred to a separatory funnel containing 4 mL 7.5 M HNO_3 and vigorously shaken. The sample was extracted again with 20 mL $CHCl_3$, and the organic phase was transferred to the funnel containing the first extract and nitric acid. After vigorous shaking, the combined organic phases were discarded, while the nitric acid extract was collected in a 20 mL Teflon beaker. The separatory funnel was rinsed with 2 mL 7.5 M HNO_3 and the rinse solution was added to the beaker. After the acid was evaporated on a hotplate, the residue was oxidized with 250 μL concentrated nitric acid. The acid was evaporated to a small droplet before being taken up with 4 mL 2 M environmental grade nitric acid. With each set of extractions (typically 21

samples), three blanks and an estuarine water reference material (SLEW-2) were processed.

2.2.3.1. Reagents

Ultrapure reagents (Seastar Chemicals Inc., Sidney, B.C.) were used to prepare 7.5 M HNO_3 and NH_4OAc buffer, while 2 M HNO_3 was made from environmental grade acid (Anachemia, Vancouver, B.C.). $CHCl_3$ (Fisher analytical grade) was cleaned by extracting twice with 5% environmental grade nitric acid. The APDC/DDDC reagent was prepared from a stock solution containing 1% w/w each of 1-pyrrolidinedithiocarbamate (Fisher Scientific Co., Fair Lawn, NJ) and sodium diethyldithiocarbamate (Aldrich Chemical Company Inc., Milwaukee, WI), stabilized in 1% NH_4OH. An aliquot was cleaned prior to use by adjusting the pH to 4 - 4.5 and extracting with 20 mL clean $CHCl_3$. The estuarine water reference material SLEW-2 was purchased from the National Research Council of Canada.

2.2.3.2. Analysis of Reference Material, Replicate Samples and Procedural Blanks

Analyses were performed on a graphite furnace atomic absorption spectrometer (Varian SpectrAA 300, Varian, Mississauga, ON) with Zeeman background correction and using platform tubes. Running parameters are given in Appendix A.1.1. Values for SLEW-2 for Cu, Cd and Zn were within the recommended range, while only 60% on average of Fe was recovered (Table 2.1). Consequently, all Fe values were recovery-corrected, and blank corrections were applied to all samples. Reduced recoveries of all

metals were observed with samples containing in excess of about 200 μg/L Cu and/or Zn.

These samples were re-analyzed without preconcentration.

	Cu	Cd	Zn	Fe
SLEW-2 found	1.50 ± 0.26 (n=11)	0.017 ± 0.002 (n=9)	1.00 ± 0.14 (n=11)	1.43 ± 0.32 (n=11)
certified	1.62 ± 0.11	0.019 ± 0.002	1.10 ± 0.14	2.37 ± 0.37
Blanks	0.077 ± 0.042 (n=15)	0.008 ± 0.004 (n=15)	0.23 ± 0.25 (n=15)	0.117 ± 0.095 (n=14)
D.L. (3σ)	0.13	0.012	0.74	0.29

Table 2.1. Analysis of the estuarine reference material SLEW-2 and of blanks using the APDC/DDDC extraction method. Concentrations in μg/L. D.L. = detection limit, calculated as three times the standard deviation of the blanks.

2.2.4. Determination of Particulate Metals

Particulate matter was collected by filtration of 250 mL water samples through acid-cleaned polycarbonate membranes (Poretics Corp., Livermore, CA, diameter 47 mm, nominal pore size 0.4 μm). The filters were folded, placed in 10 mL polyethylene vials and dried inside a plastic box in a convection oven at 60°C. The box was doubly wrapped in plastic bags. Air exchange was by means of a piece of plastic tubing fitted with a polycarbonate frit to prevent contamination by airborne particles. The dry filters were placed into 6 mL Teflon screw-cap vials (Savillex Inc., Minnetonka, MN) and 2 mL ammonia solution was added. The vials were placed on a hotplate and the ammonia was evaporated to dryness. This process completely disintegrated the filters. Next, 0.5 mL each of nitric, hydrochloric and hydrofluoric acid were added and the vials capped

tightly. The microwave digestion was performed in a carousel of twelve pressure bombs (CEM Corp., Matthews, NC) accommodating 2 vials per bomb, thus allowing to process 24 samples (including two blank filters and a sediment reference material) per run. To counteract the pressure buildup inside the vials and to keep them from popping open, the vials were placed on Teflon spacers (3 cm diameter screw-caps) and distilled water was added to just cover the spacers. After digestion (40 minutes, 40 psi) the acids were driven off by evaporation to dryness on the hotplate. The residue, a small black pellet, was redissolved in 0.15 mL nitric acid. The sample was then heated again to almost dryness and the residue was taken up in about 4 mL of 2 M nitric acid. After weighing, an aliquot of the sample was diluted with a stock solution to bring its metal concentration within a range amenable to ICP-MS analysis. The final solution was 2 M nitric acid and contained 10 μg/L In and 500 μg/L Co as internal standards along with the digested metals.

Between samples, the Teflon vials were rinsed with DDW, dried, rinsed with chloroform, wiped dry, and rinsed again with water. They were then filled with 0.5 mL each of nitric and hydrochloric acid (environmental grade), subjected to microwave digestion (40 min., 40 psi) and rinsed with DDW.

2.2.4.1. Reagents

Concentrated nitric, hydrochloric and hydrofluoric acids and ammonia solution were ultrapure grade (Seastar Chemicals Inc., Sidney, B.C.). 2 M nitric acid was prepared from analytical grade reagent (Anachemia, Vancouver, B.C.). In and Co internal standards were made from standard stock solutions (High Purity Standards, Charleston, SC and Spex Industries Inc., Edison, NJ, respectively). Marine sediment reference materials PACS-1 and BCSS-1 were purchased from the National Research Council of Canada.

2.2.4.2. Analysis of Sediment Reference Material, Replicate Samples and Filter Blanks by Microwave Digestion

Metal analysis was performed on an inductively coupled plasma mass spectrometer (VG PlasmaQuad 2+ turbo, VG Elemental, Winsford, Cheshire, U.K.) equipped with a 1 mL flow injection loop for sample introduction into a pneumatic nebulizer. Fe and Al were determined in analogue mode with Co as internal standard. Depending on their concentration, Cu and Zn were measured in either analogue (also with Co) or pulse counting mode (with In as internal standard). Cd was determined by GFAAS using the same program as for the dissolved metal. There was considerable drift in the response for Al, which had to be corrected by frequent comparison with a standard stock solution. Instrumental parameters for ICP-MS and GFAAS are given in Appendix A.1.

There are no certified reference materials for suspended particulate matter, but the values obtained with the sediment standards PACS-1 and BCSS-1 using the same procedure agree well with the certified values (Table 2.2). The only exception is Al, which gave consistently lower recoveries for BCSS. The reasons for this are unknown.

The results show that this microwave digestion technique in combination with ICP-MS (or GFAAS for some applications) is very useful in cases where small sample size precludes determination by X-ray fluorescence spectrometry (typically, less than 10 mg of sediment is needed), or when different isotopes are analyzed. The self-consistency of the results obtained with particulate metals in Howe Sound demonstrates that the technique is additionally suited for the determination of suspended particulate metals in small samples (the amount collected, not corrected for salt, was between 1 and 3 mg).

	Cu [ppm]	Cd [ppm]	Zn [ppm]	Fe [%]	Al [%]
PACS-1 found	465 ± 38 (n=8)	2.08 ± 0.1 (n=8)	811 ± 56 (n=8)	4.84 ± 0.059 (n=8)	6.68 ± 0.16 (n=8)
certified	452 ± 16	2.38 ± 0.20	824 ± 22	4.87 ± 0.084	6.47 ± 0.12
BCSS-1 found	20.5 ± 2.4 (n=15)	not measured	120 ± 9.5 (n=18)	3.18 ± 0.129 (n=18)	5.16 ± 0.59 (n=12)
certified	18.5 ± 2.7		119 ± 12	3.29 ± 0.098	6.26 ± 0.22
Blank filters	0.42 ± 0.29 (n=11)	0.015 ± 0.015 (n=11)	0.38 ± 0.13 (n=11)	3.0 ± 1.8 (n=11)	2.4 ± 1.3 (n=11)
D.L. (3σ)	0.86	0.046	0.38	55 x 10^{-3}	39 x 10^{-3}

Table 2.2. Analysis of sediment reference materials PACS-1 (Esquimalt Harbour, B.C.) and BCSS-1 (Baie des Chaleurs, Qué.), and of blank filters using the microwave digestion method. Metals were determined by ICP-MS, except blanks and Cd in PACS-1 by GFAAS. Blanks and detection limits (D.L.) are reported for a 10 mg sample of sediment. For particulate matter collected by filtration of 250 mL of water the detection limits translate to 0.034 (Cu), 0.0018 (Cd), 0.015 (Zn), 0.21 (Fe) and 0.15 (Al) μg of particulate metal per litre of sample.

2.3. Results

2.3.1. Behaviour upon Mixing

2.3.1.1. The Need for Standardization

The conservative or non-conservative behaviour of metals during estuarine mixing is commonly determined using concentration-salinity plots as described by Boyle et al. (1974) and Liss (1976). In this so-called reactant approach it is assumed that salinity is a conservative tracer of mixing between freshwater and salt water. The concentration of conservative constituents will plot linearly with salinity, since they are not affected by processes other than physical dilution.

The reactant approach was used with the entire dataset gathered from twelve monthly surface transects in an attempt to determine seasonal variation in the mixing behaviour of metals. The example with Cu (Figure 2.1) shows that there is a very wide range of surface seawater salinities and of initial metal concentrations in the creek. Synoptic interpretation of the data in terms of conservative or non-conservative behaviour is almost impossible, and there is a great need for standardization of the plotting parameters.

The y-axis can be normalized by expressing metal concentrations as a percentage of the initial creek concentration:

$$\%\left(M_{creek}\right) = 100 \frac{[M]_{d,n}}{[M]_{d,c}}$$ (2.1)

where $[M]_{d,n}$ = dissolved metal concentration at site n along the surface transect

        $[M]_{d,c}$ = dissolved metal concentration in the creek
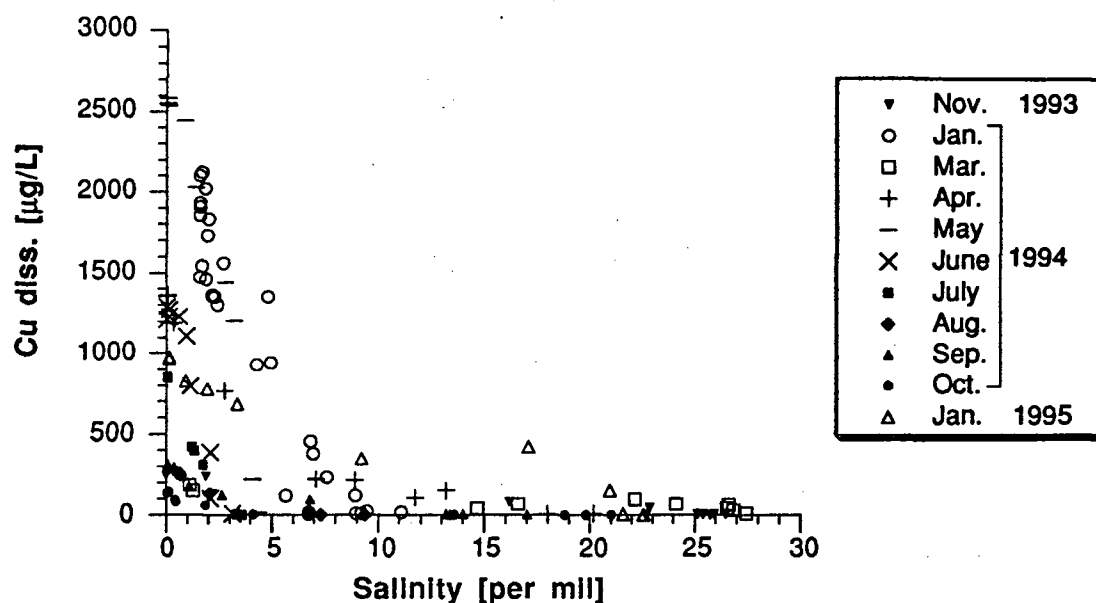
Figure 2.1. Dissolved Cu concentrations in 12 surface transects taken between November 1993 and January 1995. The symbols are grouped according to seasons, where closed symbols represent summer/fall, open symbols are used for winter, and +, − and x are spring samples.

In the case of iron, the concentrations in the seawater end-member are not negligible and have to be accounted for:

$$\%(Fe_{creek}) = 100 \frac{[Fe]_{d,n} - MI_n[Fe]_{d,s}}{[Fe]_{d,c}}$$ (2.2)

where MI_n = mixing index at site n

$[Fe]_{d,s}$ = dissolved iron concentration in the seawater end-member

The mixing index, a measure of the amount of mixing between freshwater and salt water that has taken place at site n, will be defined in Section 2.3.1.2.

The x-axis could be standardized in a similar fashion, but as will be shown, salinity does not represent a conservative index of mixing in the system under consideration due

to the presence of an additional end-member (Squamish River), hence the proportion of mixing will have to be defined using a different parameter.

2.3.1.2. A Conservative Index of Mixing other than Salinity

Concentration-salinity plots for Cd (Figure 2.2) could be interpreted as showing seasonally variable behaviour, with removal in April, release in May and conservative behaviour in January. Conservation of mass demands that any decrease (or increase) in dissolved Cd be reflected in an increase (or decrease) in particulate Cd, assuming that there is no significant removal of Cd via rapidly sinking particles, which in fact is the case as will be shown in Section 2.4.1. Ratios of particulate to total Cd (Figure 2.3) show that the particulate fraction comprises less than one percent of the total, except in the marine end-member, where particulate Cd amounts to up to six percent of the total. The low particulate Cd concentrations relative to the dissolved imply that the particulate fraction acts as neither a significant sink nor source for dissolved Cd. In other words, Cd behaves essentially as a conservative element. (A more detailed appreciation of the conservative nature of Cd is given in Section 2.4.1). As a consequence, in the absence of large-scale removal via rapid sedimentation, the observed removal/release patterns (Figure 2.2) must be artefacts, most likely caused by lateral advection of surface water in Britannia Bay, which results in a variable seawater end-member. Thus, a conservative tracer of mixing is needed that is not affected by the presence of more than one marine end-member.

Since Cd behaves conservatively and is greatly enriched in Britannia Creek water over seawater (mean enrichment 70-fold, range 4- to 310-fold), it can be used as a tracer of mixing. In analogy to the concentration *versus* salinity plots commonly used, concentration *versus* dissolved Cd plots can be used to determine the behaviour of metals
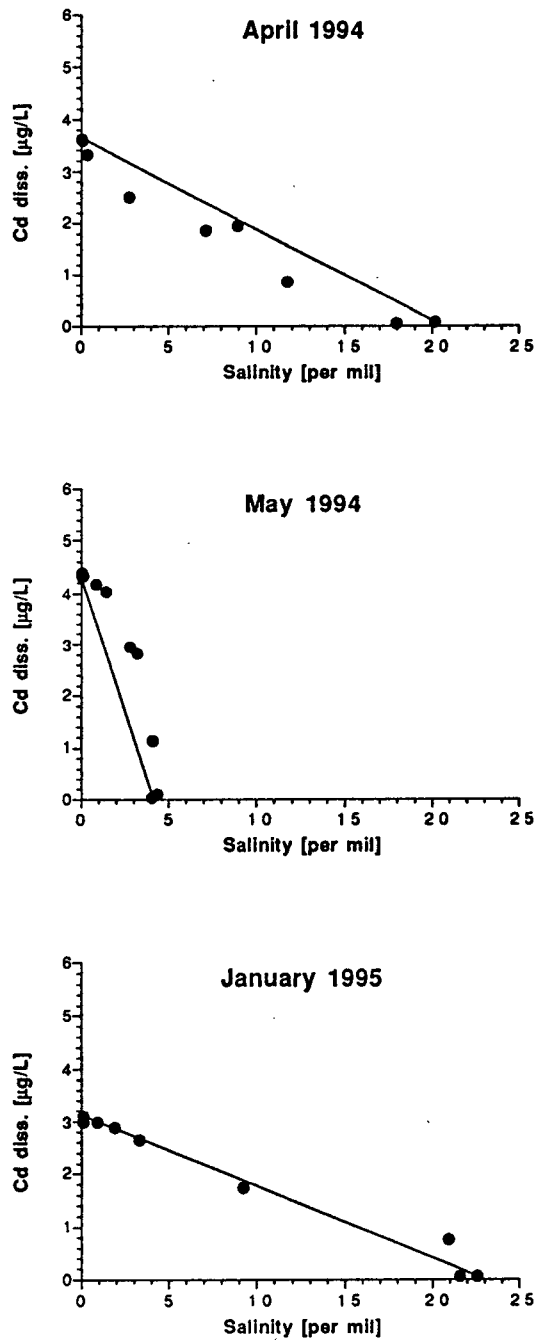
Figure 2.2. Dissolved Cd in three transects collected in April and May 1994 and in January 1995. Also shown is the conservative mixing line.

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during estuarine mixing. As pointed out in Section 2.3.1.1., it is useful to normalize the x-axis, so that data can be more easily compared. A Cd-based mixing index (MI) is therefore defined as follows:

$$MI_n = \frac{[Cd]_n - [Cd]_c}{[Cd]_s - [Cd]_c} \qquad (2.3)$$

where $[Cd]_n$ dissolved Cd concentration in sample n

         $[Cd]_c$ "   "   "   in creek

         $[Cd]_s$ "   "   "   in seawater

The mixing index could be corrected for the higher percentage of particulate Cd in seawater samples, but since high salinity samples have a mixing index close to unity by definition, the error introduced is negligible for our purposes.
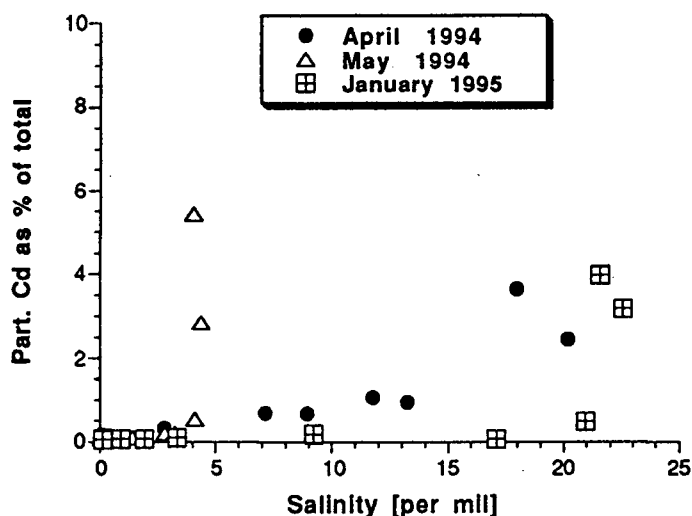
Figure 2.3. Percentage of total Cd present as particles > 0.4 μm in the same transects as shown in Figure 2.2.

2.3.1.3. Metal Distributions as a Function of Mixing Index

The mixing behaviour of dissolved Cu is shown in Figure 2.4. By using the mixing index and by expressing Cu concentrations as fraction of the Cu present in the creek, all the data can be displayed in a coherent manner despite large seasonal variations in surface seawater salinity (range 3.12 - 27.4‰) and in Cu concentrations in the creek (range 150 - 2580 μg/L). Cu behaved in a non-conservative fashion throughout the year, and no seasonal trends in the extent of removal are apparent. The February 1994 data (excluded from Figure 2.4) showed a much more pronounced drop in metal concentrations at low salinity, however these samples were collected just after a severe rainstorm and do not represent normal conditions.

Zinc (Figure 2.5) generally exhibited conservative behaviour during the entire year. Again, the February data did not follow the trend for the reasons mentioned above. Dissolved Fe in Britannia Creek ranged from 7.0 to 354 μg/L and was generally lower than dissolved Zn and Cu, sometimes by over an order of magnitude. During periods of low Fe in the creek, the seawater Fe concentration was of similar magnitude (range 3.7- 38.9 μg/L). In order to demonstrate the behaviour of creek-iron even at times when the creek signal was obliterated by large seawater Fe concentrations, all concentrations in Figure 2.6 were corrected for this seawater contribution. Removal of iron was observed throughout the year. Since removal occurs in the early stages of mixing (i.e. at MI ≤ about 0.4), corresponding to a reaction time of a few minutes, it is also very rapid. Both observations are in line with a vast body of evidence from the literature suggesting that removal of Fe during mixing is an ubiquitous feature of its estuarine chemistry (e.g. Boyle et al. 1974, Sholkovitz et al. 1978, Hong and Kester 1985. See also Table 3.1 for additional references).
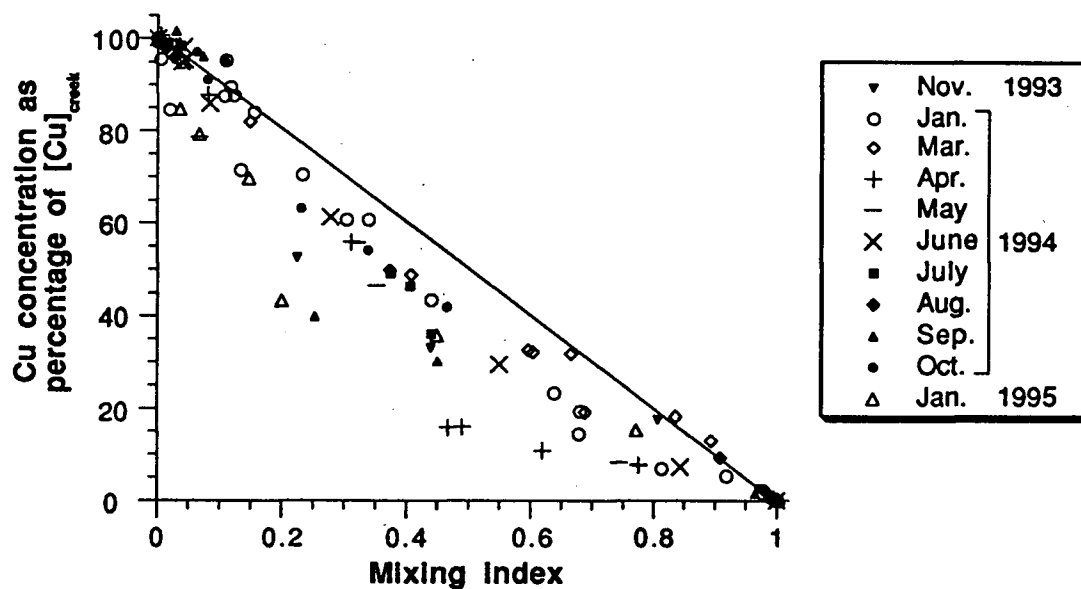
Figure 2.4. Dissolved Cu concentrations, normalized to the initial concentration in the creek, *versus* Cd-based mixing index. This figure shows the same data as Figure 2.1 plotted on normalized axes. Again, the symbols are grouped according to seasons, where closed symbols represent summer/fall, open symbols are used for winter, and +, − and x are spring samples.
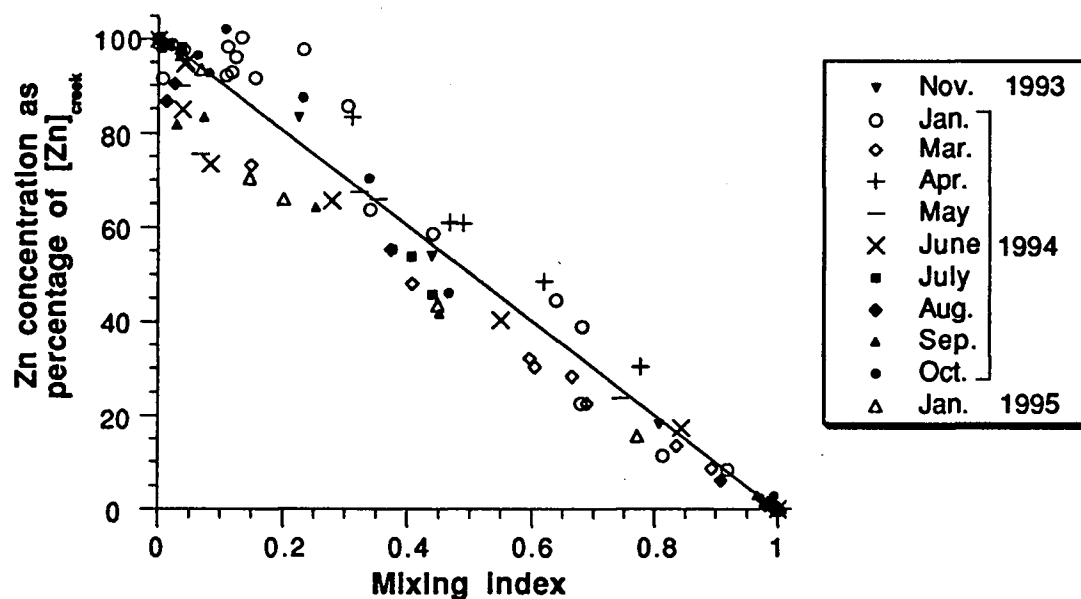
Figure 2.5. Percentage of creek-derived dissolved Zn *versus* mixing index. Symbols as in Figure 2.4.
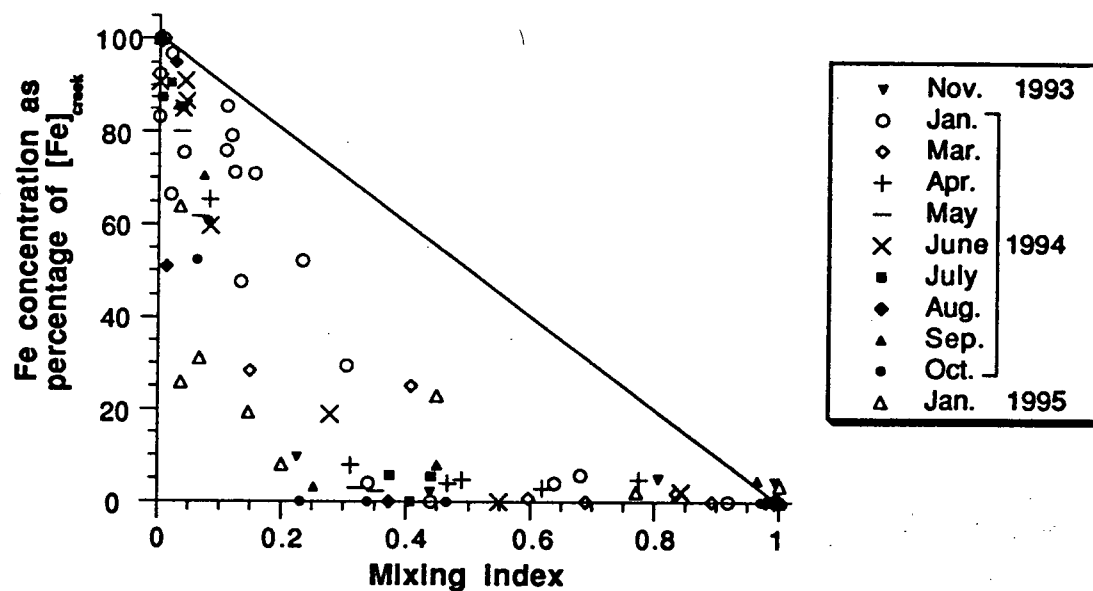
Figure 2.6. Percentage of creek-derived dissolved Fe *versus* mixing index. Symbols as in Figure 2.4.

2.3.2. Dispersion in the Estuary

Salinity and temperature profiles at the distal Station A (for location refer to Figure 1.1, Chapter 1) show the typical oceanographic features of a mid-latitude fjord. Surface runoff from the Squamish River produces a thin lens of fresher surface water overlying an intermediate layer of higher salinity, while the deep waters exhibit uniform temperature and salinity year-round (Figure 2.7). In this coastal environment, density is determined by salinity rather than by temperature, due to the large salinity contrast between surface and deep waters, which gives rise to a pronounced pycnocline at shallow depth. Surface salinity is lowest during freshet, and at about the same time surface temperatures rise as a result of increased insolation. An increase of the salinity of the subsurface layer is observed in the spring, which may be a result of changing water properties of the water flowing in from outside the sill.

Dissolved Cu, Cd and Zn vary over a broad range according to their respective inputs from marine sources and mine discharge (Table 2.3). Concentrations at the surface are generally higher and vary more than those at depth. Also, Cu and Zn concentrations exceed Cd at the surface by two orders of magnitude, which agrees with their relative abundances in the ore and in acid mine drainage.

Depth		Cu	Cd	Zn
0 m	mean	13	0.15	17
	range	1.3 - 68	0.039 - 0.76	1.7 - 58
> 10 m	mean	1.9	0.074	2.9
	range	0.45 - 8.8	0.056 - 0.12	0.70 - 15

Table 2.3. Mean and range of dissolved Cu, Cd and Zn concentrations at Station B over the entire sampling period. Concentrations in μg/L.
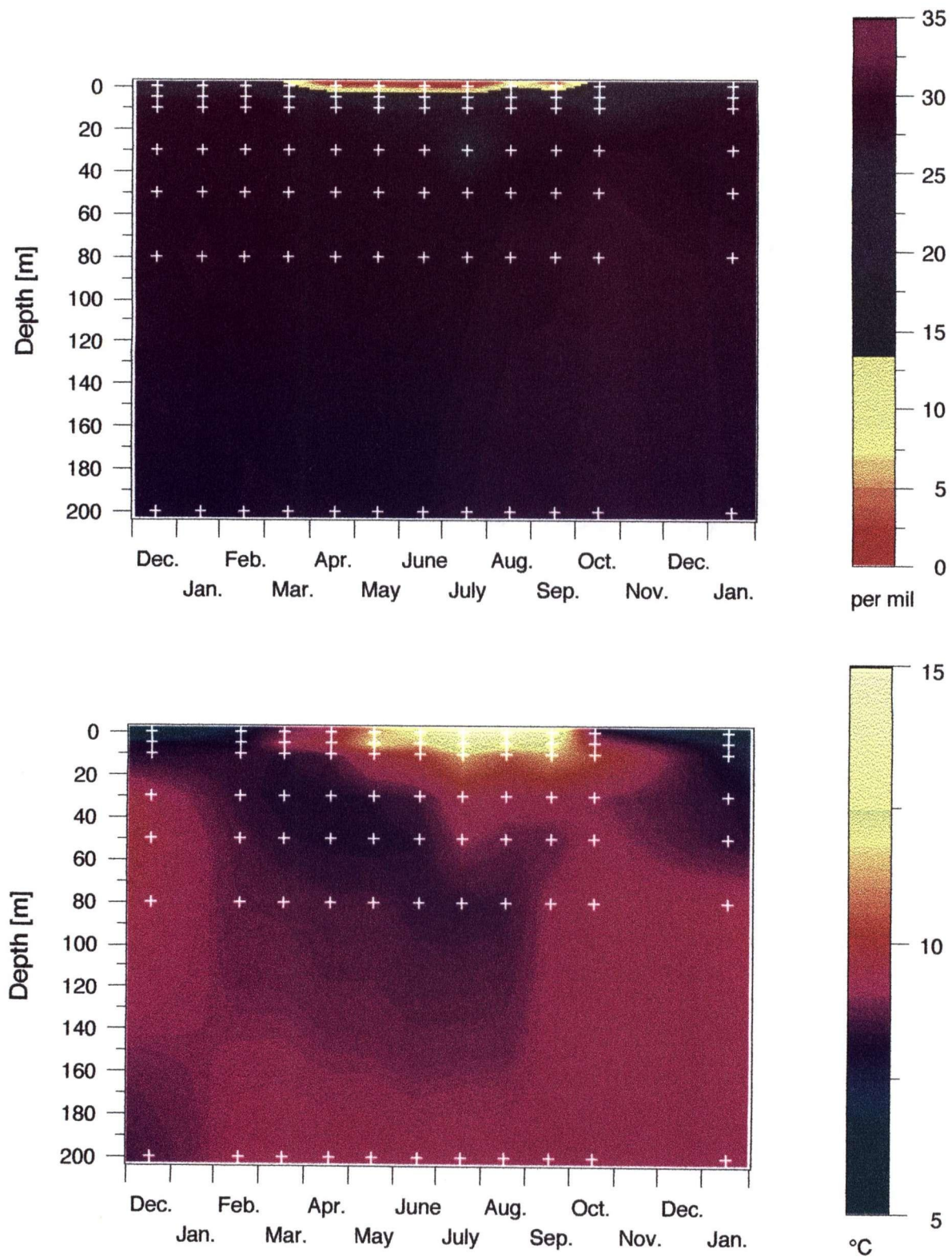
Figure 2.7. Salinity (top) and temperature (bottom) at the offshore Station A for the period November 1993 through January 1995. Profiles at Station B, which is closer to the mine, are virtually the same. Bottom depth is 240m.

Vertical profiles of Cu (Figure 2.8) emphasize the contrast between high concentrations at or close to the surface and more uniform low concentrations in the deeper waters. At the site close to the mine (Station B, for location refer to Figure 1.1, Chapter 1) high surface concentrations reflect high metal loads in the Britannia Creek discharge from January through June. With lower creek flows in summer, both discharge and metal concentration in the creek decline, resulting in a shrinkage of the surface plume and low metal concentrations at this site. A second maximum at 10 m depth is observed in June, July and August, presumably caused by the discharge of AMD through the submerged outfall. It is unlikely that the maxima between 30 and 50 m depth observed in April and July are a result of surface or subsurface discharge of AMD-containing freshwater, since it would need a higher density than the surrounding seawater to sink to these depths. On the other hand, the maxima are observed at both Stations A and B and are defined by more than one data point each, so that they appear to be real. Concentrations are lower at the site farther from the mine (Station A), which may indicate that they represent some mine-related signal. During operation of the mine, tailings were deposited on the steep flanks of the basin in the vicinity of the mill. The possibility of slope instabilities causing mine tailings to slide off the flanks was discussed by Syvitski and Macdonald (1982) and by Drysdale (1990), who cites anecdotal evidence for the occurrence of such processes. A slumping event could certainly cause high suspended particulate Cu and Zn concentrations, which through dissolution and presence of colloidal particles may have contributed to the temporary maxima between 30 and 50 m depth.

The offshore site A does not reflect all of the features observed at site B. Most notably, the spring surface maximum of dissolved metals is absent, which may be due to a general attenuation of metal concentrations with increasing mixing (distance) from the mine, or to this station being located in the Squamish River outflow during freshet. High surface water dissolved Cu concentrations were observed at Station A in January 1994 even though at Station B concentrations were low. In the absence of strong wind and tidal
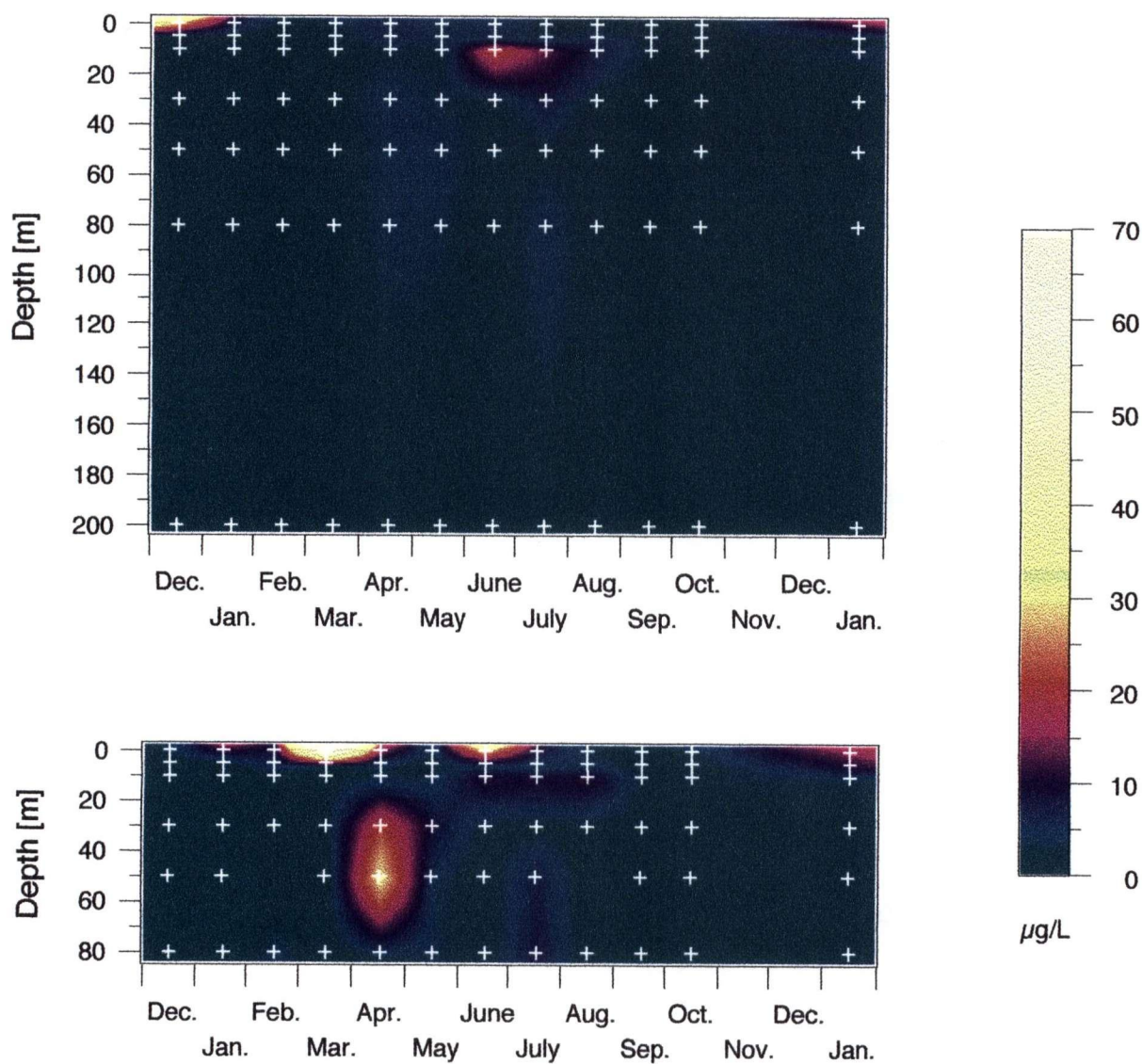
Figure 2.8. Dissolved Cu concentrations in μg/L at the offshore Station A (top) and at the site close to the mine (Station B, bottom) for the period November 1993 through January 1995. Bottom depths are 240 m and 100m, respectively.

currents, the creek plume is deflected northward and moves along the shore until it meets the estuarine surface outflow in the area of Watts Point (Figure 1.1, Chapter 1) (Buckley and Pond 1976). If these circumstances were present during sampling, the creek plume would have bypassed Station B but not Station A.

Vertical profiles of dissolved zinc (Figure 2.9) are almost identical to those of Cu, and their congruence is evidence for the common source of the metals. Minor differences can be observed in surface waters, where Zn concentrations sometimes exceed those of Cu (e.g. January and July 1994). This may reflect changes in the Cu/Zn ratio in the creek (compare also Figure 2.14) and the lesser removal of Zn in the mixing zone relative to Cu.

Dissolved Cd profiles also match the distributions observed with Cu and Zn (Figure 2.10). It is interesting to note that in the spring and summer dissolved Cd concentrations at the surface were actually lower than in the deeper, saltier waters since during these times Britannia Creek water (which has low Cd levels compared to Cu and Zn) mixes predominantly with Cd-poor Squamish River runoff rather than with seawater.

Dissolved iron concentrations at depth at both Stations remain below about 10 µg/L through most of the year (Figure 2.11). While with Cu, Cd and Zn a maximum attributed to submarine discharge of metals was observed during the summer months at or below 10 m, no such feature is visible with Fe. Rapid removal of Fe has been observed in surface waters, and it is likely that removal is also fast in deep waters, leading to low concentrations at depth. For the same reason, the surface maximum reflects the seawater concentration rather than the input of iron-rich Britannia Creek water. This is particularly true in March and July, when dissolved Fe concentrations in the creek (40 and 63 µg/L, respectively) were of the same order of magnitude as Fe in estuarine surface waters (21 and 52 µg/L at Station A, respectively). The near-bottom maximum in January 1994 could be caused by contamination upon collection, but since dissolved Zn (which is also very easily contaminated) does not show a maximum and since high particulate Cu/Zn

ratios (which are an indicator of mine-derived metal) were observed at this depth, the feature could also be real. However, it does not appear to be caused by resuspension since particulate Cu, Zn, Fe or Al are not elevated relative to other months as would be expected in such a case.
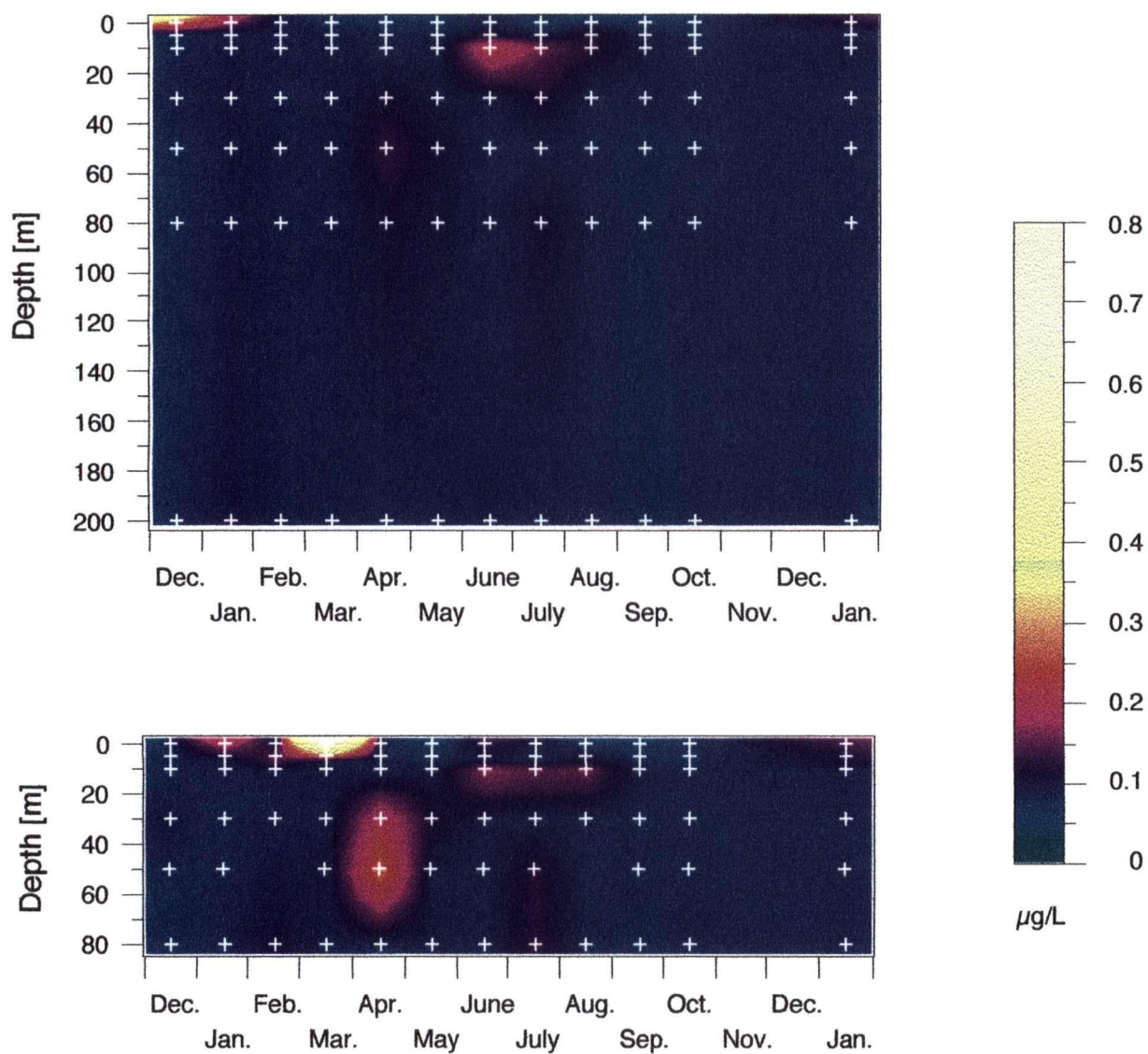
Figure 2.9. Dissolved Cd concentrations in µg/L at the offshore Station A (top) and at the site close to the mine (Station B, bottom) for the period November 1993 through January 1995. Bottom depths are 240 m and 100m, respectively.
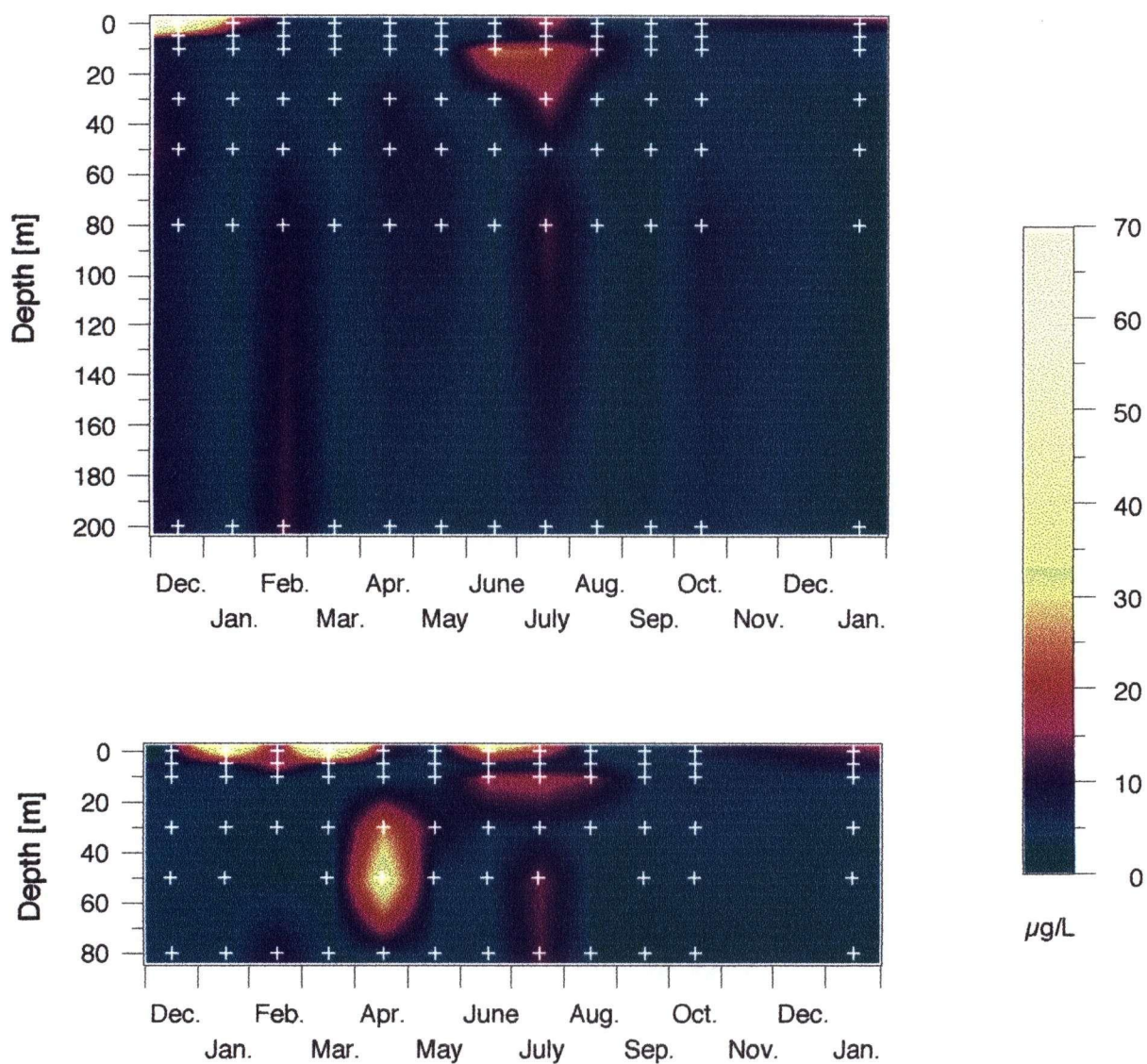
Figure 2.10. Dissolved Zn concentrations in μg/L at the offshore Station A (top) and at the site close to the mine (Station B, bottom) for the period November 1993 through January 1995. Bottom depths are 240 m and 100m, respectively.
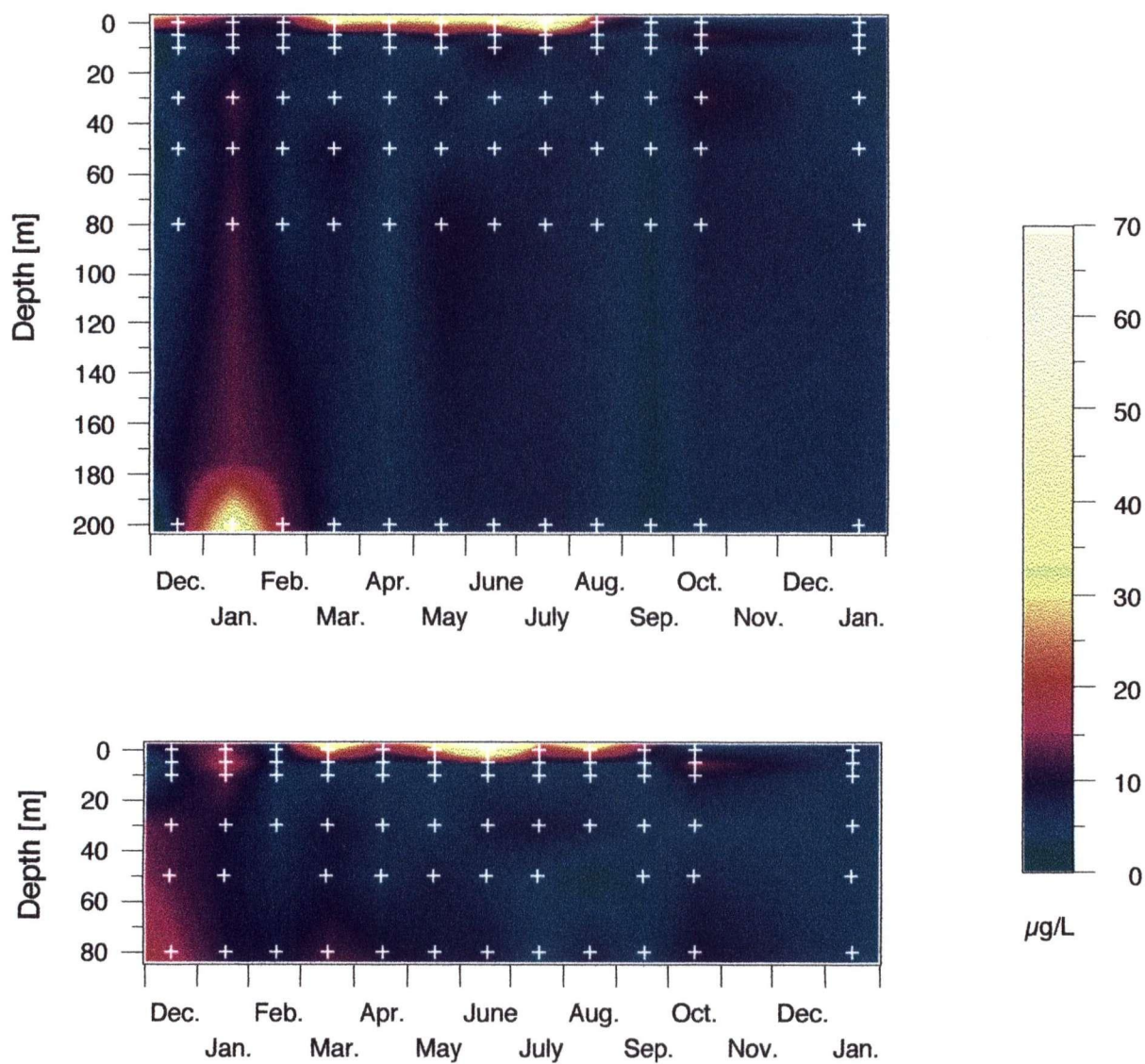
Figure 2.11. Dissolved Fe concentrations in μg/L at the offshore Station A (top) and at the site close to the mine (Station B, bottom) for the period November 1993 through January 1995. Bottom depths are 240 m and 100m, respectively.

2.3.3. Vertical Transport

The vertical transport of metals was investigated using sediment trap moorings. Cu fluxes at the distal site A were smaller than at the site close to the mine (Figure 2.12 a) and remained approximately constant with depth. At the same time, particulate matter fluxes increased with depth (Figure 2.12 b), indicating a deep source of particulate matter, for example resuspended material from the flanks of the fjord. In contrast to Cu, Zn fluxes were similar at the two sites (Figure 2.12 c) and increased with depth in a similar fashion as the particulate matter flux, suggesting that the settling particulate Zn at both sites represents mostly detrital material.

a)

Depth [m]

Cu flux [mg/m²/day]

Station A
Station B
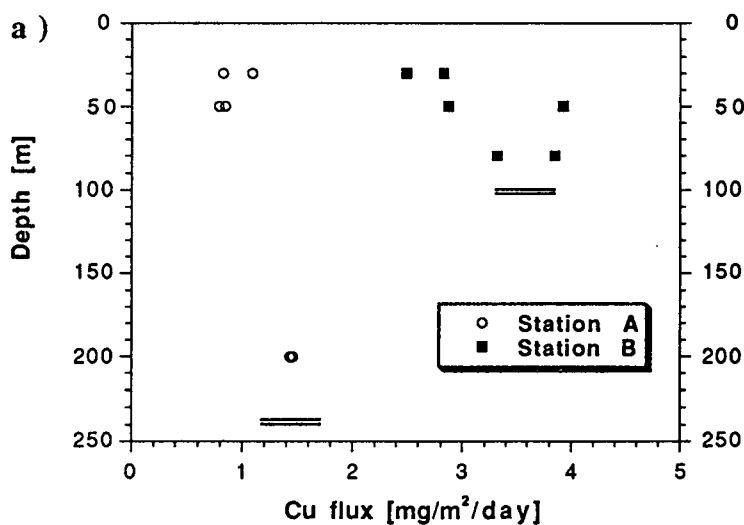
Figure 2.12. (continued next page)
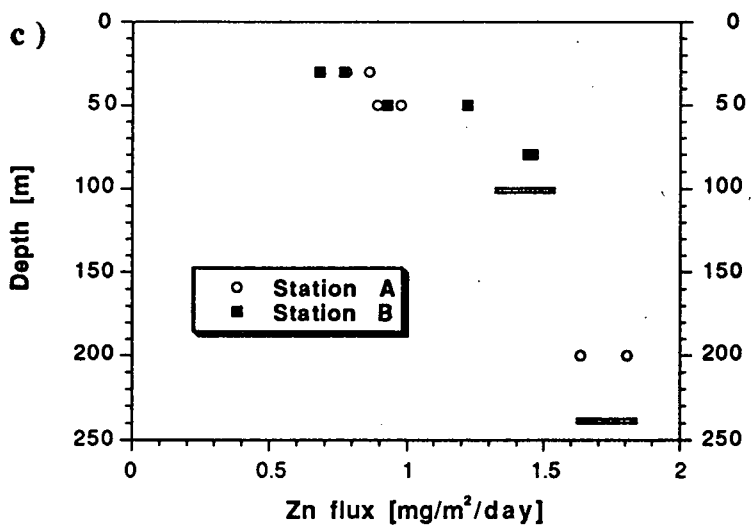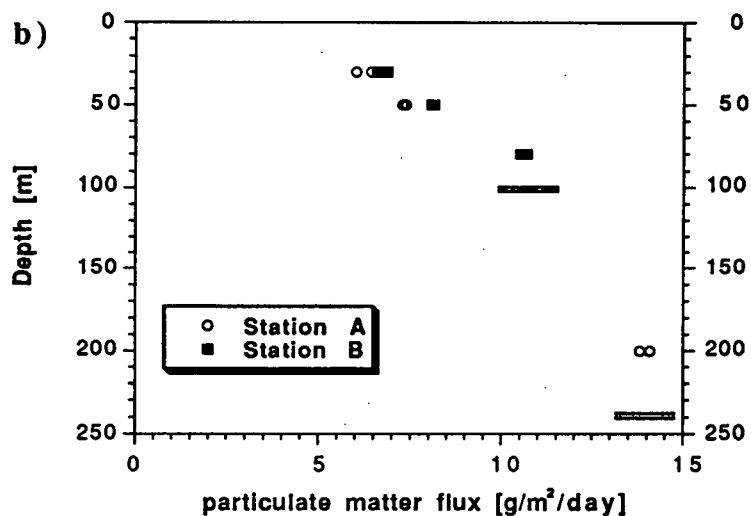
Figure 2.12. Fluxes of a) Cu, b) particulate matter and c) Zn in sediment traps deployed during December 1993 and January 1994. Traps were hung in pairs, one of each contained formaldehyde as a preservative. Bottom depths at the two sites are shown with double lines.

2.4. Discussion

2.4.1. Use of Cd a Conservative Tracer of Mixing

The conditions under which salinity-concentration plots may not be useful to determine conservative behaviour have long been recognized. Boyle et al. (1974) pointed out that apparent non-conservative distributions can result from the presence of a third end-member. Loder and Reichard (1981) demonstrated that apparent non-conservative behaviour of normally conservative constituents can also be caused by temporal variations in end-member concentrations. Officer (1979) emphasized that the model is only valid in steady state, one-dimensional conditions. Given the considerable lateral variations in both metal concentrations and salinity that are observable in Howe Sound, the assumption of one-dimensionality is questionable.

The presence of a third end-member in the form of the submerged outfall could be responsible for apparent release patterns such as the one observed in May for Cd (Figure 2.2). However, as will be shown later, the subsurface discharge remains trapped below the pycnocline for part of the year. When surfacing in winter, higher metal concentrations are observed only at the lower end of the mixing zone, and do not alter the Cd distribution at lower salinities.

Temporal variations in creek metal concentrations could also be responsible for the apparent non-conservative behaviour of Cd. In order to produce the removal pattern observed in April shown in Figure 2.2, a decrease of dissolved Cd concentrations in the creek of 30% during the one-hour collection period would be required. Similarly, the release observed in May would require a 30% increase. Detailed studies on the short-term variability of metal concentrations are lacking, but natural fluctuations of this magnitude seem unlikely.

In contrast, variability in the salinity of the marine end-member could well explain the observed behaviour. There is a considerable degree of lateral inhomogeneity in surface water properties in Britannia Bay brought about by wind- and tide-induced changes in circulation patterns. These result in variable degrees of mixing between Squamish River water and seawater. Lateral inhomogeneity is also evident from surface metal concentrations as discussed in Section 2.4.4.1. A conservative tracer of mixing other than salinity is therefore required for the interpretation of metal behaviour during estuarine mixing.

The assumption of conservative behaviour of Cd as inferred from its partitioning between dissolved and particulate phases would not hold true if there was significant transport of Cd by large, rapidly sinking particles. This particle pool could be underrepresented in field samples due to collection artefacts. Mixing experiments with unfiltered Britannia Creek and Howe Sound water were performed to test this (see Chapter 3). The advantage of mixing experiments over field data is that they consider the entire particle pool, even the rapidly sinking ones. The results showed that less than 1% of the Cd originally present flocculated upon mixing. Hence, even if all of this flocculated Cd was removed from the mixing zone via rapidly sinking particles, dissolved Cd would still essentially behave in a conservative manner.

Further support for the conservative nature of Cd can be derived from the congruence argument made by Chapman et al. (1983). Following their reasoning, the more parameters that are congruent (i.e. the more metals that have the same concentration distribution along the course of mixing) are observed, the more likely they are controlled by dilution and not by chemical reactions. Dissolved Cd in Howe Sound surface samples shows excellent covariance with dissolved Zn (Figure 2.13). Cd and Zn have similar chemical properties and could well be governed by the same chemical reactions during estuarine mixing. The congruence of the two metals alone does not prove their

conservative nature, but together with the relative scarcity of particulate Cd it lends more support to the notion that Cd might be a better tracer of mixing than salinity.
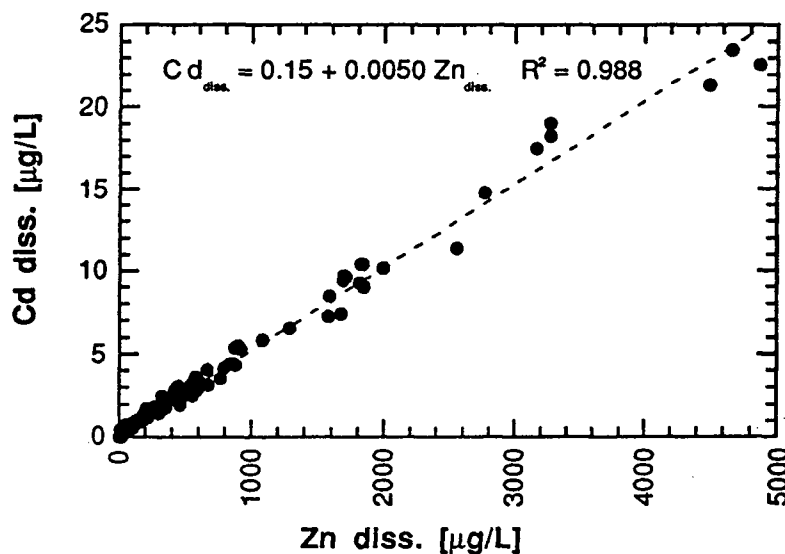
Figure 2.13. Correlation between dissolved Cd and Zn in surface samples. These data cover the entire dataset of transects, including samples from the upper reaches Britannia Creek (Section 3.3.2), and the surface samples from the vertical profiles.

The congruence argument could be expanded to include total metal concentrations. In the absence of large-scale removal of metals from the mixing zone by rapidly sinking particles, the sum of particulate and dissolved metal concentrations should be controlled only by dilution. Plots of total concentrations *versus* a conservative tracer of mixing such as dissolved Cd or the Cd-based mixing index should result in a straight line. Figure 2.14 shows that this is in fact the case within the analytical precision. The linear behaviour provides further support for the conservative nature of Cd, and it also implies that particulate Cu, Zn and Fe essentially remain suspended in the mixing zone.
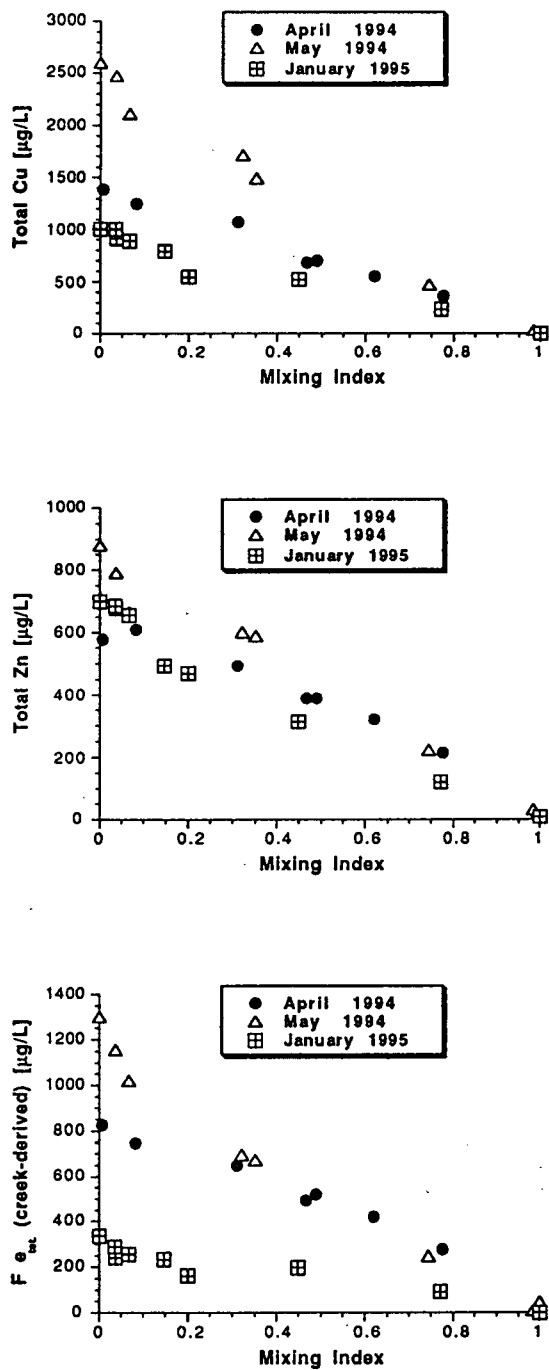
Figure 2.14. Total concentrations of Cu (top), Zn (centre), and Fe (bottom) in selected surface transects. Fe was corrected for contributions from the seawater end-member.

2.4.2. Seasonality of Metal Discharge to Howe Sound

While there appears to be little seasonal variability in metal removal in the mixing zone as suggested by the normalized concentration *versus* MI plots (Figures 2.4, 2.5, 2.6), there is however a pronounced seasonal dependence of metal delivery to the system as shown in Figure 2.15. Total Cu, Cd and Zn concentrations in Britannia Creek were high in winter, decreased in early spring, reached another maximum in late spring and gradually declined towards fall. This seasonal variability is a result of the hydrological regime of the system, as will be discussed presently.

There are no discharge records for Britannia Creek, but an estimate can be obtained by scaling the flow measured at the neighbouring Stawamus River, adjusting for the size of the respective catchment areas (29 and 40.4 km^2 for Britannia Creek and Stawamus River, respectively, Steffen, Robertson and Kirsten 1991). Since the median elevation of the two basins is comparable (1150 and 1090 m, respectively, Steffen, Robertson and Kirsten 1991), there should be no large differences in the proportion of meltwater that the two creeks carry at any given time. Figure 2.16 shows the dependence of Britannia Creek discharge on both precipitation and snowmelt. Often there is a rapid response to rainfall events, particularly in fall and early winter. In contrast, discharge during spring and early summer does not reflect precipitation patterns and appears to be mostly meltwater-fed.

The seasonal pattern observed in metal concentrations (Figure 2.15) and in creek discharge (Figure 2.16) is accentuated in metal loadings (Figure 2.17). While metal concentrations span one order of magnitude, metal loadings vary over two orders of magnitude. This accentuates the pronounced seasonality of metal discharge to Howe Sound beyond that noted earlier.

The coincidence of concentration and discharge maxima in Britannia Creek implies that an increase in creek discharge has to be accompanied by an even larger increase in metal delivery from the mine. This can be explained by considering the potential for
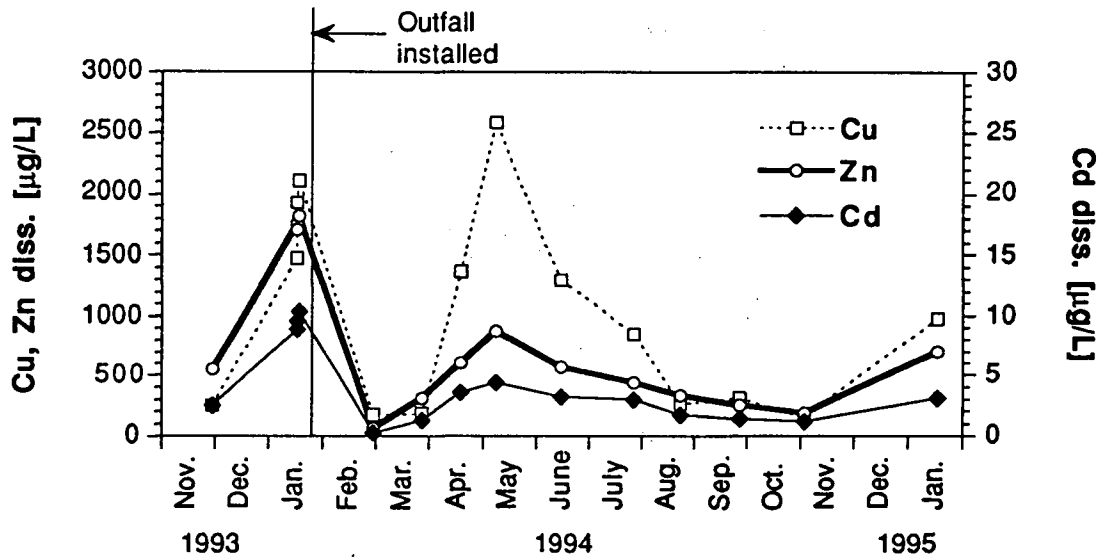
Figure 2.15. Total Cu, Cd and Zn concentrations (in µg/L) in Britannia Creek for the period from November 1993 through January 1995. Particulate Cu accounted for 1 - 40% of the total Cu load, while particulate Cd and Zn contributed less than 2%. Acid mine drainage emanating from the 4100 portal was routed through a submerged outfall after January 18, 1994, which resulted in lower concentrations in Britannia Creek. Pre- and post-installation concentrations are thus not directly comparable.

metals to accumulate within the mine during dry periods. Most of the acid mine drainage appears to be generated within the underground workings. The water that flows through the system enters the mine primarily through open pits situated at high elevations (Steffen, Robertson and Kirsten 1991). During summer, the products of the oxidative dissolution of the ore accumulate within the underground workings in stagnant water or as soluble salts on drying rock surfaces. With increased precipitation in the fall, more water flows through the mine, and the accumulated acid mine drainage gets flushed out, leading to a first peak in metal concentration in the creek. As precipitation falls as snow at higher elevations later in the year, water-flows through the mine again decrease, and acid mine drainage collects within the mine. Upon spring snowmelt in the mountains,
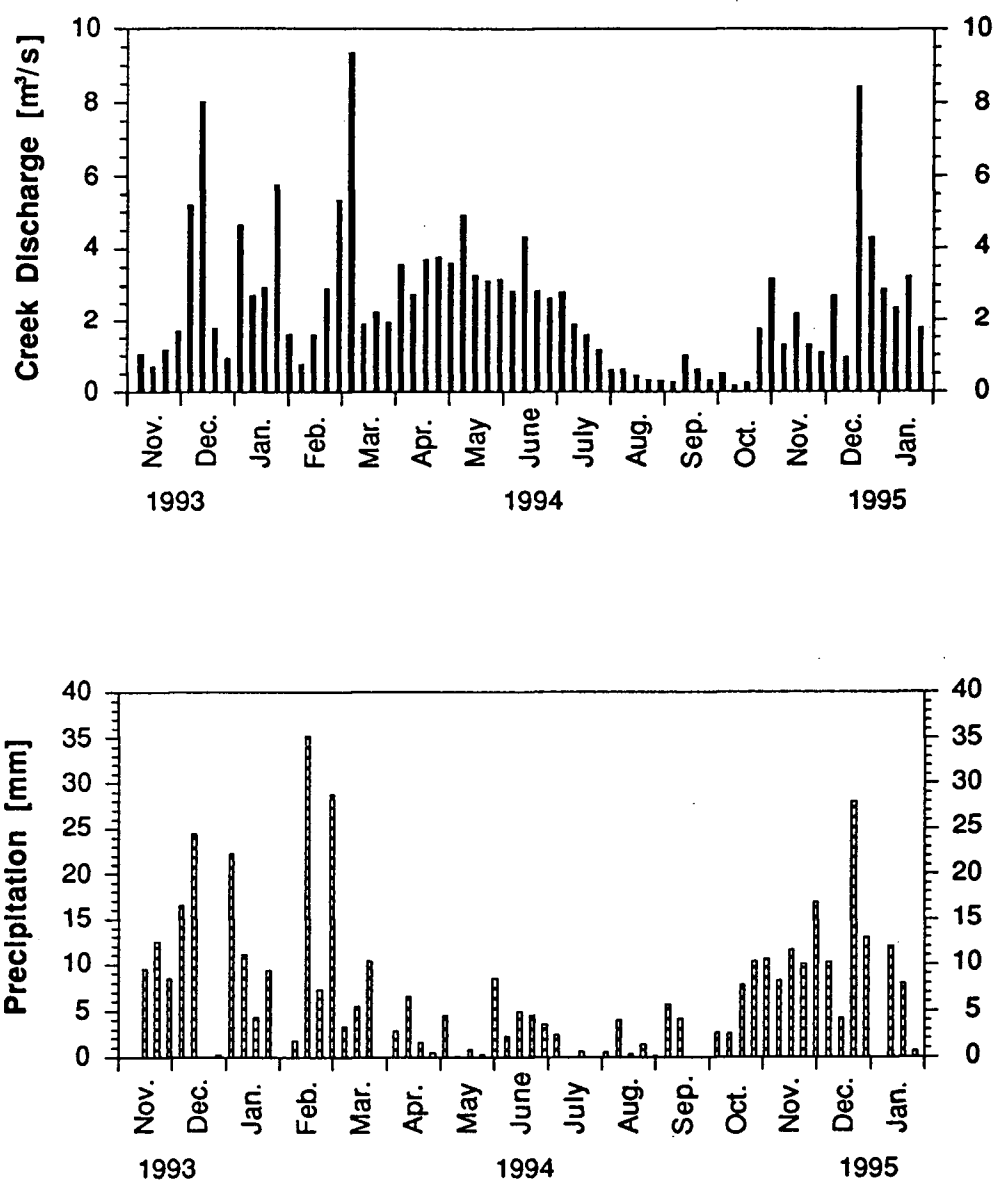
Figure 2.16. Weekly mean discharge of Britannia Creek (top) estimated from Stawamus River flow records, and weekly mean precipitation at Squamish Airport (bottom).
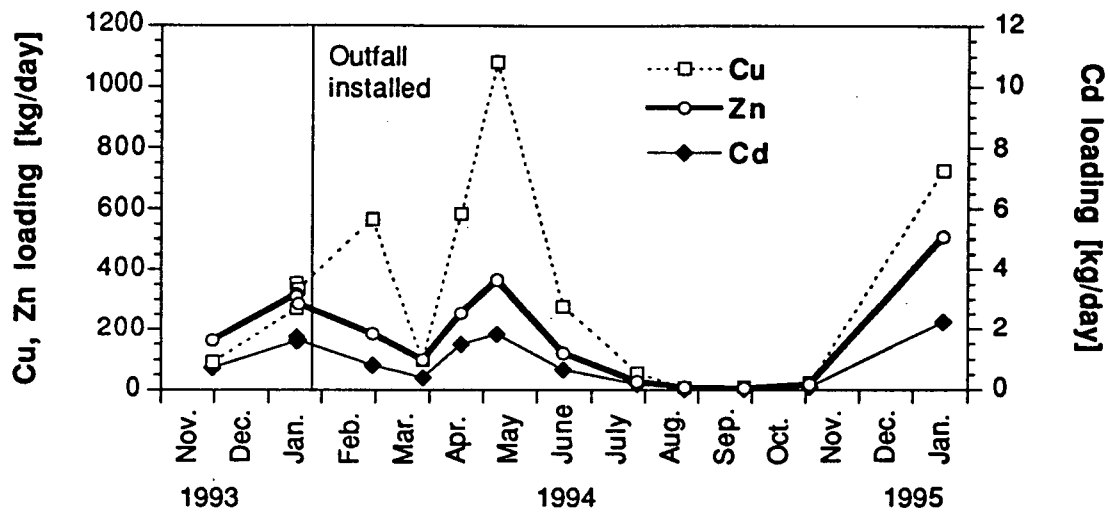
Figure 2.17. Loadings of total Cu, Cd and Zn in Britannia Creek as calculated from the total metal concentrations (Figure 2.15) and creek discharge (Figure 2.16). The peak observed with Cu in February likely reflects high suspended particulate matter loads from soil erosion and washout of precipitated Cu in the creek bed following a severe rainstorm.

large amounts of water enter the mine and lead to a second maximum in creek metal concentrations. Similar flushing mechanisms are commonly invoked in the literature to explain elevated metal concentrations during periods of high discharge (e.g. Walling and Foster 1975, Johnson and Thornton 1987, Robertson 1990), although the maxima in discharge and concentrations do not always coincide (Robertson 1990).

Measured flows at the 4100 portal (Figure 2.18), which is one of the two main exit points for mine waters, show that in fact seasonal discharge patterns of Britannia Creek and water flowing through the mine are quite similar. The mine does not respond as much to rainfall events, possibly because during periods of heavy rain most of the water runs off as sheet flow rather than penetrating into the mine. Metal concentrations at the 4100 portal do not vary much except for iron, which appears to be regulated by pH (Fig. 2.19).
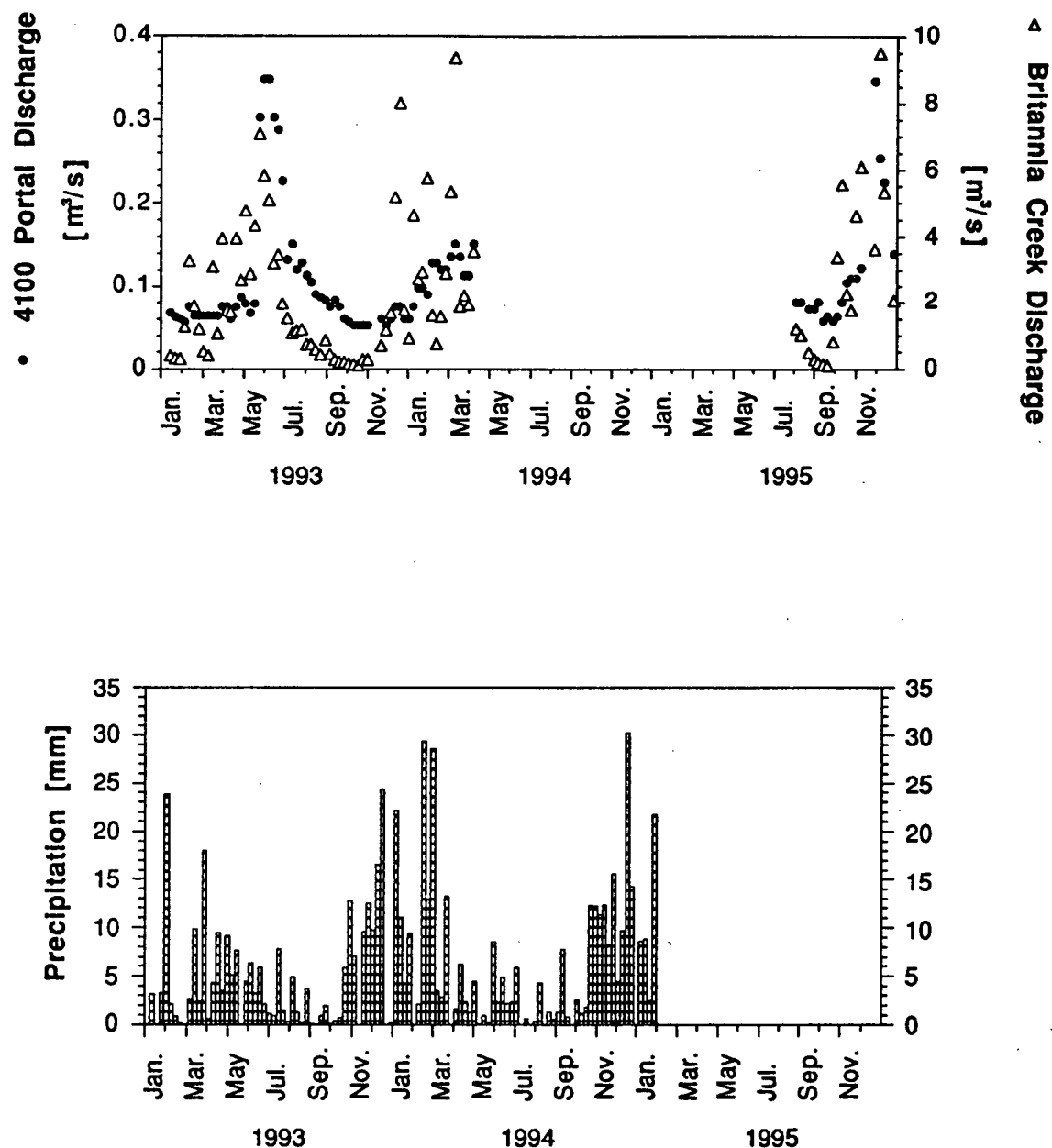
Figure 2.18. Discharge at the 4100 portal and at Britannia Creek (top) and weekly mean precipitation at Squamish airport (bottom). The 4100 portal data were obtained from weekly flow gauge readings for the period from January 1993 through December 1995. No readings were taken at the 4100 portal between April 1994 and July 1995. Britannia Creek discharge is the weekly mean, estimated from Stawamus River streamflow gauges. Note that the peaks in 4100 discharge have no correspondence in precipitation, suggesting that they are controlled primarily by meltwater. Britannia Creek in contrast reflects both storm events and snow melts.

Thus the metal load of the AMD is governed primarily by water flow and exhibits peaks in late spring and winter. This pattern was also observed by examination of Cu loading records in 1982 -1984 (Goyette and Ferguson 1985). Metal concentrations in Britannia Creek prior to installation of the submerged outfall were therefore controlled primarily by the proportions of creek and 4100 portal discharge. During periods of high runoff, metal concentrations in the creek were additionally elevated by the input of acid mine drainage at the 2200 portal situated further upstream of Britannia Creek. Although comparable in terms of metal load during periods of high runoff, the limited data available suggest that this source is less important relative to the 4100 discharge under low flow conditions (Price et al. 1995). Since January 1994, the 2200 drainage has been the primary source of AMD to Britannia Creek owing to the direct discharge of the 4100 drainage at depth in Howe Sound. It is also interesting to note that the relative proportions of Cu, Cd and Zn in the acid mine drainage are not constant, reflecting the heterogeneity of the ore body. As a result, the proportions of these metals in the creek also vary with time (Figure 2.15).

The hydrologies of the mine and of Britannia Creek not only control metal concentrations in the creek, but can also explain some of the seasonal variability observed in pH, particulate Fe and particulate Al (Figure 2.20). pH is low in winter and spring when runoff and dissolved metal concentrations are high, reflecting increased input of acid mine drainage. Particulate Fe and Al are roughly inversely correlated with pH (with the exception of February), which points to increased precipitation of these metals at high pH. Precipitation of insoluble iron and aluminum oxides and sulphates from solution with rising pH is a well-documented phenomenon in acid mine drainage environments (e.g. Barton 1978, Chapman et al. 1983, Brady et al. 1986, Karlsson et al. 1987, Sullivan et al. 1988). Particulate Fe and Al concentrations are additionally controlled by a detrital component from suspended terrigenous particulate matter which at times of high turbidity may greatly exceed the amount contributed by chemical precipitation. This is likely the reason for the high values observed in February (Figure 2.20).
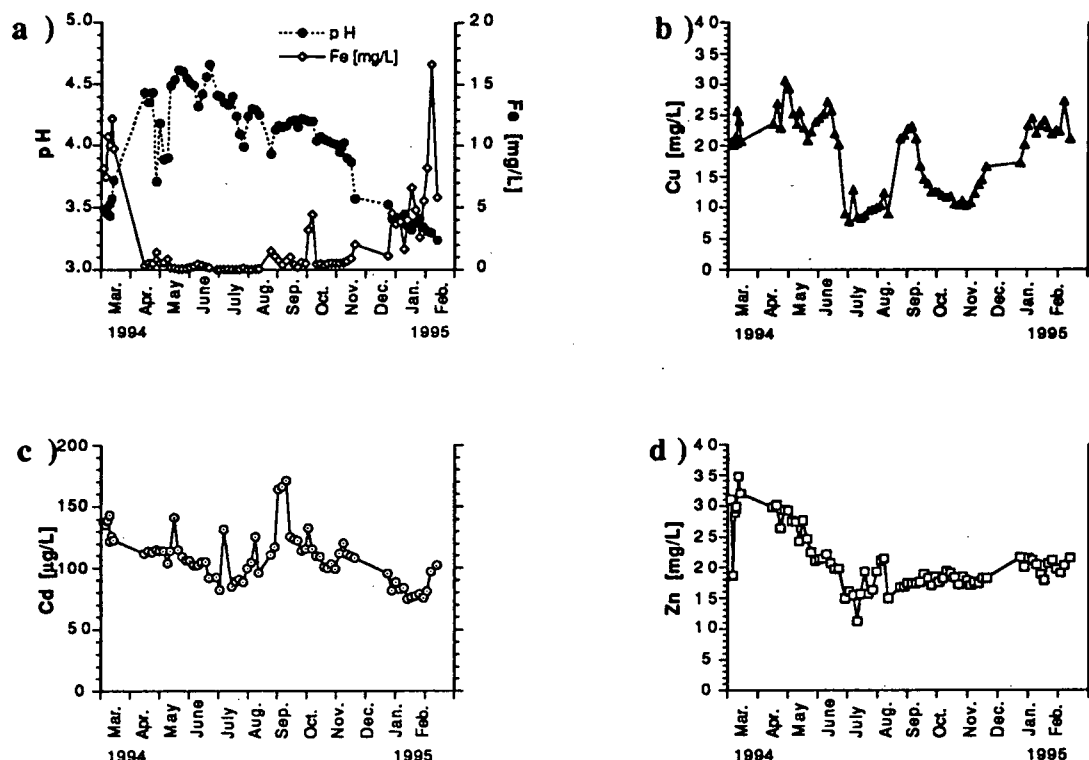
Figure 2.19. a) pH and Fe, b) Cu, c) Cd and d) Zn in 4100-portal discharge. Total metal concentrations are in mg/L, except Cd in µg/L.

Surface-seawater salinity and silt content (Figure 2.21) in contrast are not controlled by the hydrology of Britannia Creek but by the Squamish River discharge, which is larger in the summer by over two orders of magnitude. The Squamish is to a large extent meltwater-fed, which results in low flows in winter and high flows during freshet (Figure 2.22). The river typically takes on a milky appearance in spring due to high loads of suspended silty material derived from glaciers, which in turn gives rise to the high particulate Al concentrations in Howe Sound surface waters during freshet.
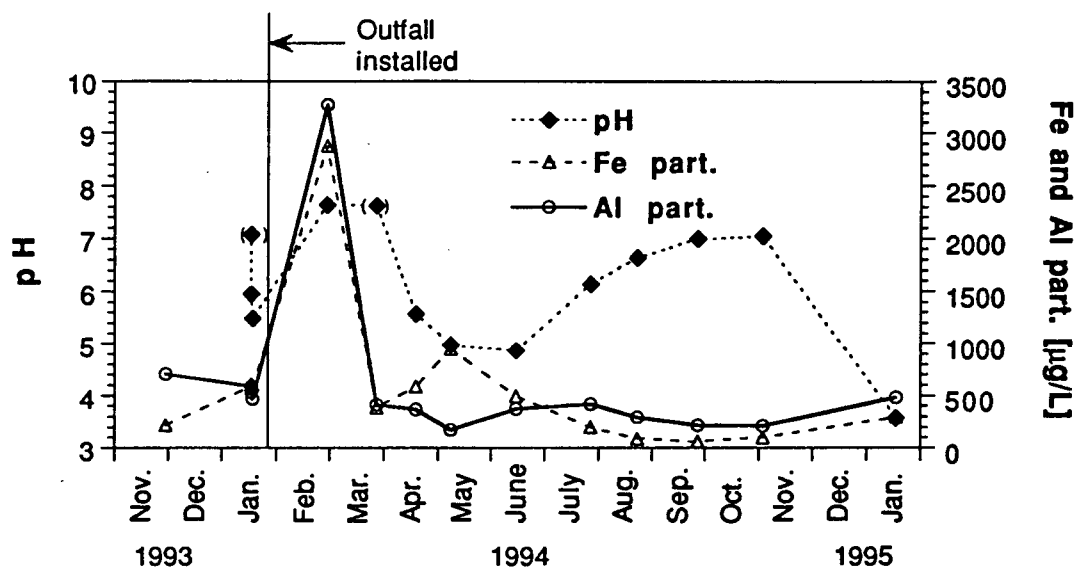
Figure 2.20. Particulate Fe and Al (in µg/L solution), and pH in Britannia Creek for the period from November 1993 through January 1995. The bracketed values indicate rejected data due to malfunctioning of the field pH meter. As in Figure 2.15, the time of installation of the submerged outfall is shown.
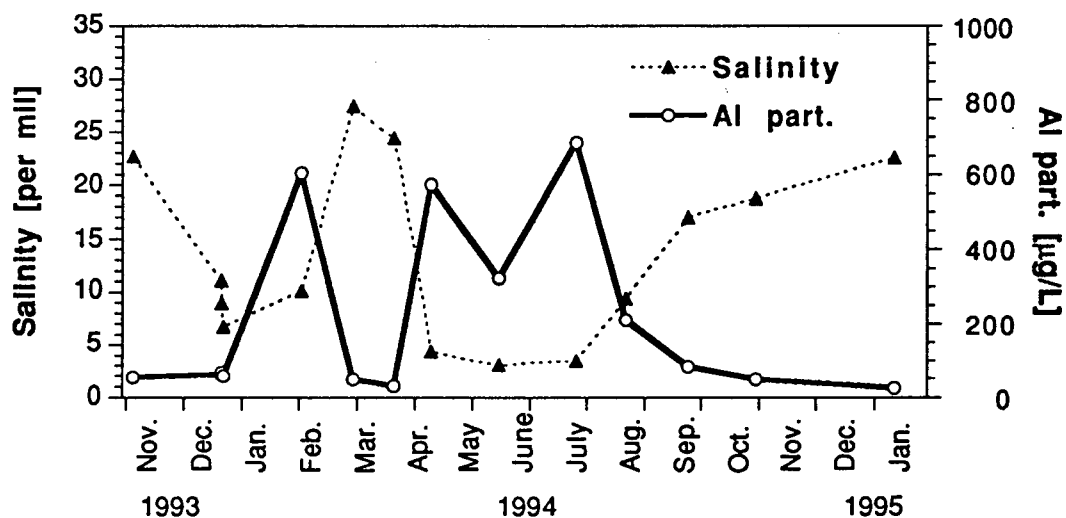
Figure 2.21. Particulate Al (in µg/L) and salinity in the marine end-member of surface transects. Al is used as a proxy for suspended silt and clay.
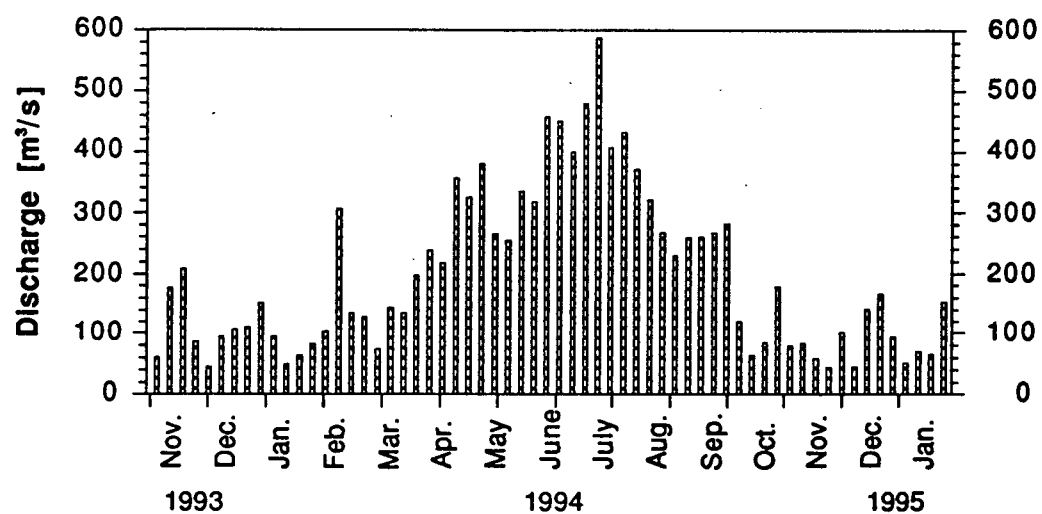
Figure 2.22. Weekly mean Squamish River discharge from automated stream flow gauges.

2.4.3. Seasonality of Metal Removal in the Mixing Zone

The behaviour of dissolved Cu, Cd, and Zn in the mixing zone is rather uniform throughout the entire year (Figure 2.6, 2.7). Considering the large temporal variability in pH, silt content, salinity, particulate Fe and Al, and dissolved metal concentrations, this consistency is unexpected. For example, a rise in pH could enhance metal removal by oxidation of ferric iron and precipitation of iron and aluminum oxyhydroxides (Sullivan et al 1988, Stumm and Morgan 1996), which may serve as adsorption sites for other metals (Benjamin and Leckie 1981a and 1981b, Balistrieri and Murray 1982, Tessier et al. 1996). Alternatively, high pH could cause the direct removal of metals via formation of insoluble oxides (Stumm and Morgan 1996). Increased turbidity could also enhance removal of metals, since clays have been reported to adsorb Cu, Cd and Zn (Pavlova and Sigg 1988), and adsorption of Cd onto quartz has been observed by Benjamin and Leckie (1982). Metal removal through aggregation and coagulation of metal-bearing particles (Krone 1978) or through adsorption of metals onto particles (Balistrieri and Murray 1982) may be enhanced by high salinity, or more precisely by increased concentrations of divalent cations such as Mg and Ca (Eckert and Sholkovitz 1976, Sholkovitz and Copland 1981, Balistrieri and Murray 1982). From all this evidence, it would appear that the behaviour of Cu, Cd and Zn in the mixing zone should be affected by seasonal factors at least to some extent. It will become evident that there are in fact seasonal changes, but due to the predominance of the dissolved phase, they are recognized only when the particulate fraction is considered.

Particulate Cd and Zn in the mixing zone generally make up < 1% and a few percent of the total metal concentration, respectively. In contrast, particulate Cu can contribute from 1 to 70% to the total, often comprising around 40%. Even with Cd and Zn, however, the proportion of the particulate fraction is not constant across the mixing zone. Instead, it shows a maximum at intermediate dilution with salt water, suggestive of metal removal.

The implication is that while the bulk of the metal behaves conservatively, there is a small fraction that is reactive during mixing. The removal of dissolved Cu, as implied by increasing particulate metal concentrations at intermediate dilution, is seasonally variable, as shown with selected examples in Figure 2.23. Cd and Zn removal in contrast is small and more constant over time.

For mass balance calculations, it is important to know the extent of metal removal during different times of the year. The concentration of metal flocculating can be calculated from particulate metal data:

$$[M]_{flocc.} = [M]_{p,n} - [M]_{p,c}(1 - MI_n) - [M]_{p,s}MI_n \qquad (2.4)$$

where $[M]_{p,n}$ = particulate metal concentration at a site n along the transect

$[M]_{p,c}$ = particulate metal concentration in the creek

$[M]_{p,s}$ = particulate metal concentration in seawater

MI_n = mixing index at site n

As shown in the hypothetical idealized transect (Figure 2.24), the concentration of flocculated metal reaches a maximum around MI = 0.5. Since we want to know the amount of metal removed upon complete mixing, not its concentration, these values need to be converted by multiplying by the dilution factor, which can be defined as $1/(1-MI_n)$ for the special case of 1 L creek water being mixed with seawater. The percentage of metal removed upon mixing is then obtained as:

$$\%flocc. = 100\% \times \frac{[M]_{flocc.,n} \times 1/(1 - MI_n)}{[M]_{d,c}} \qquad (2.5)$$

where $[M]_{flocc.,n}$ = flocculated metal concentration at a site n along the transect

$[M]_{d,c}$ = dissolved metal concentration in the creek
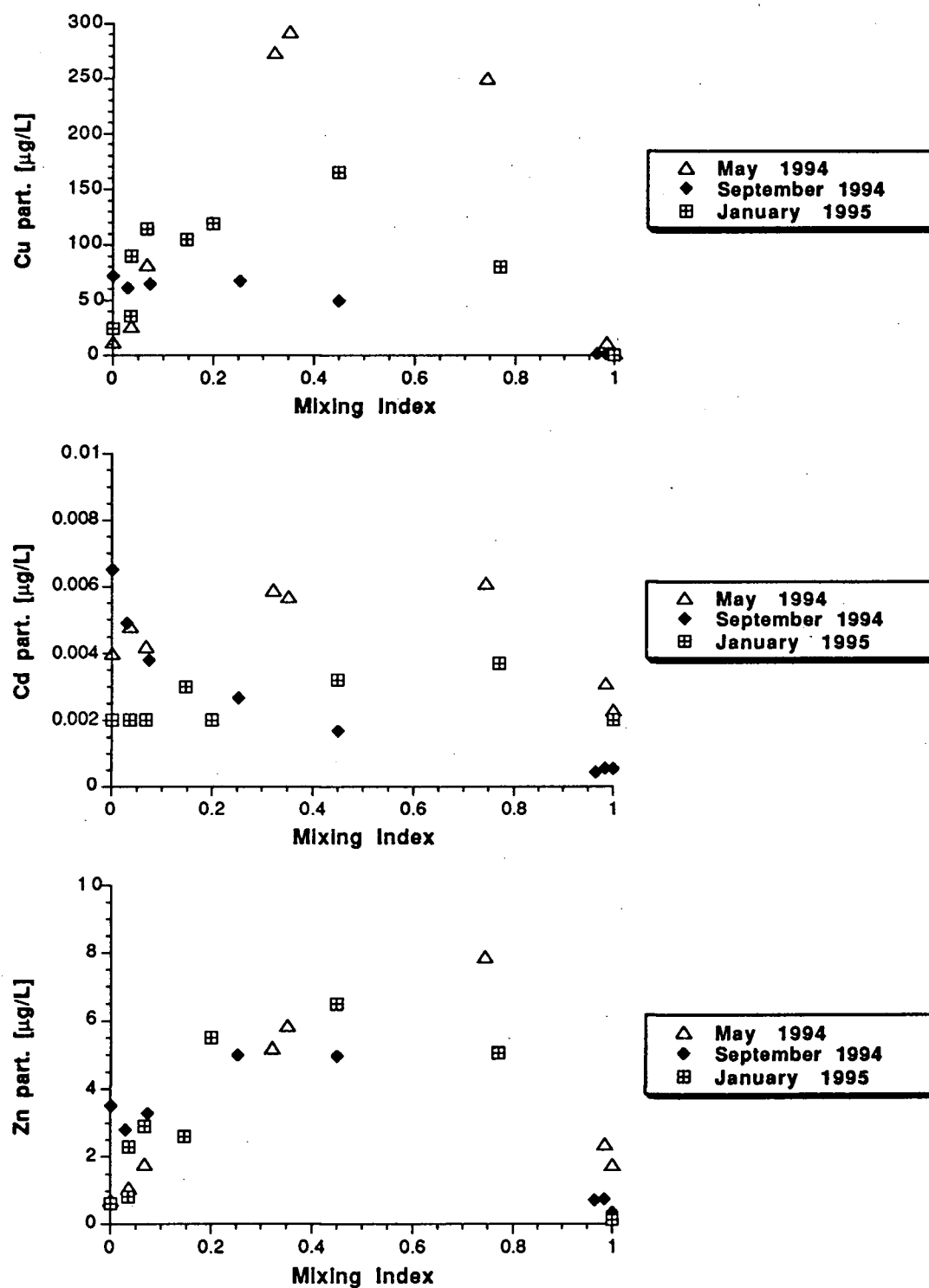
Figure 2.23. Particulate concentrations of Cu (top), Cd (center) and Zn (bottom) in μg/L *versus* Cd-based mixing index in three transects collected in May and September 1994 and in January 1995. Note that even in the case of Cd the two axis are independent, since particulate Cd is not used in the calculation of the mixing index.
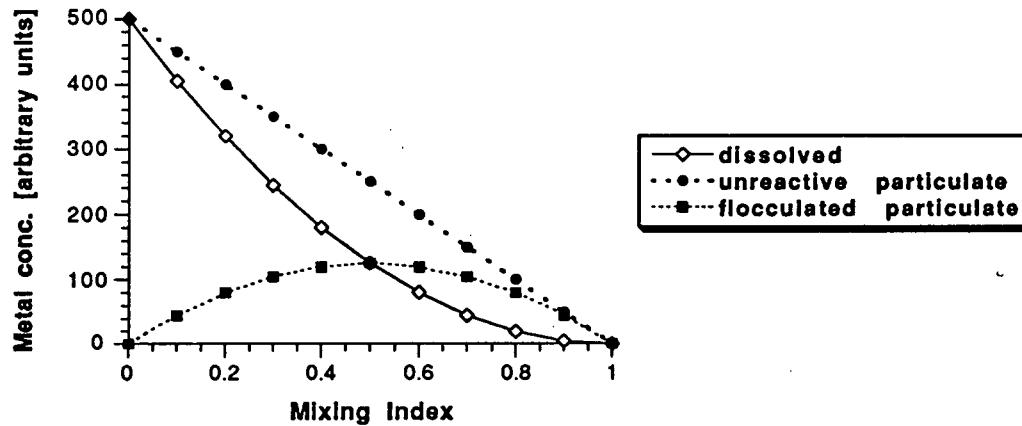
Figure 2.24. Behaviour of different metal fractions upon mixing with salt water in an ideal scenario. Dissolved metal is assumed to be subject to removal during mixing. The particulate fraction is divided into two pools, an unreactive particulate fraction representing creek particles that are subject only to dilution, and a flocculated particulate fraction resulting from the removal of metal from the dissolved phase.
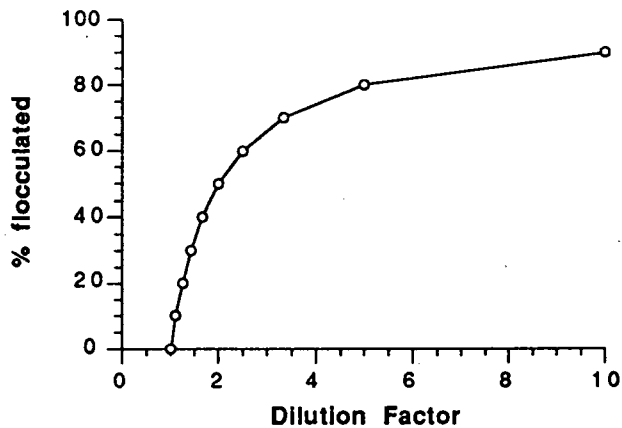
Figure 2.25. Percentage of metal flocculated for the scenario in Figure 2.24 *versus* dilution factor. For calculation of removal efficiency see text.

When plotted against the dilution factor, the percentage of metal flocculated increases asymptotically towards infinite dilution (Figure 2.25). The removal efficiency can be approximated from the maximum percentage of metal flocculated at high dilutions. A more precise estimate could be obtained by determining the asymptotic value at infinite dilution, which is not possible using the available data since very good resolution at MI -> 1 is needed.

Dataset	% Cu flocc.	% Cd flocc.	% Zn flocc.
Nov. 1993	56	0.34	5.5
Jan. 1994 H1	34	0.10	0.61
Jan. 1994 H2	29	0.12	3.8
Jan. 1994 L	32	0.13	2.9
Feb. 1994	≈ 0	≈ 0	≈ 0
Mar. 1994	≈ 0	≈ 0	15
Apr. 1994	82	0.71	25
May 1994	37	0.30	2.8
June 1994	49	0.42	4.3
July 1994	20	≈ 0	1.6
Aug. 1994	≈ 0	≈ 0	1.2
Sep. 1994	≈ 0	≈ 0	9.0
Oct. 1994	38	-0.37	3.0
Jan. 1995	33	0.24	3.0

Table 2.4. Percentage of metal removed during mixing, relative to the dissolved concentration in the creek. The negative value indicates release into solution, while ≈ 0 denotes instances where no removal or release could be calculated. Note that even though dissolved and particulate Cd are linked to each other mechanistically, they are treated as independent variables here. This is justified since calculation of the mixing index is based on dissolved Cd alone, while particulate Cd was assumed negligible owing to its low concentration. The calculations would give the same results if Zn was used for calculating the mixing index. H1, H2 and L denote replicates at first high tide on Jan. 17, second low tide on Jan. 17, and first high tide on Jan. 18, 1994.

The data presented in Table 2.4 emphasize some of the points made earlier. Cu is removed to a considerable extent during most of the year, while the fraction of Zn removed is small, and Cd behaves essentially as a conservative element. No removal is observed for any of the three metals in February, which again points out the uncommon conditions encountered during sampling. Removal in April seems excessively high, although the reasons for this are not known. Copper flocculation varies over a wide range, from no observable removal in late winter and fall to about 50% in June and November. Calculated removal efficiencies of replicate datasets (HS 0194 H1, H2 and L) are quite consistent, suggesting that the observed variability is a real feature and not a sampling or analytical artefact. The maximum amount of Cu removed appears to be closely dependent on the initial Cu concentration in the creek, since a linear relationship

$$[Cu]_{flocc., max. (ng)} = -46 + 0.37[Cu]_{diss., creek} \quad R^2 = 0.93 \tag{2.6}$$

was found (April data excluded). This correlation not only implies that more Cu flocculates when its concentration in the creek is high, but also, since the intercept is non-zero, that if dissolved Cu drops below about 124 μg/L in the creek, there is no measurable removal of Cu to the particulate phase. The dependency on creek concentrations is evidence that Cu removal may be controlled by the precipitation of insoluble oxides. At high Cu concentrations, the solution may be oversaturated with respect to insoluble phases such as $Cu(OH)_2$, resulting in spontaneous precipitation of Cu. During certain times no measurable removal of Cu is observed, which may be due to lack of precipitation as a result of undersaturation or kinetic hindrance. These issues will be addressed in detail in Chapter 3.

Similarly, with Zn a linear relationship between the amount of Zn removed and its dissolved concentration in the creek is found (April data excluded):

$$[Zn]_{flocc., max. (ng)} = 1.7 + 0.03[Zn]_{diss., creek} \quad R^2 = 0.87. \tag{2.7}$$

Cd behaves in a similar fashion as Cu with very little removal or even release in summer and fall. There is no analogous correlation between the amount of Cd removed and dissolved creek Cd concentrations, although this may reflect limitations of the data (concentrations are often close to the detection limit) rather than absence of removal.

The correlations between amount of metal removed and concentration in the creek found for Cu and Zn are important, since they permit calculation of the attenuation of metal inputs to Howe Sound by removal processes in the mixing zone. The lack of a similar relationship with Cd is not a major concern since the amount flocculated is less than one percent, and removal of Cd in the mixing zone will not measurably affect the amount delivered to the estuary via Britannia Creek.

2.4.4. Seasonality of Metal Dispersion in the Estuary

2.4.4.1. General Features of Metal Dispersion

The characteristic shallow sill and substantial freshwater input of this fjord-type estuary lead to the typical two-layered flow and the establishment of a well pronounced pycnocline at shallow depths. Ultimately, it is this physical oceanography which is responsible for the mechanism of metal dispersion in Howe Sound. Mine effluent discharged to the surface cannot mix with deep waters because of the presence of a strong pycnocline year-round. Instead, it mixes with the relatively fresh waters in the surface layer which may be as shallow as 3 m during periods of low runoff. In well-mixed and partially mixed estuaries, pollutants added at the surface frequently get diluted considerably by physical mixing with the large volume of water that the estuary represents. This is not the case in a fjord, since the volume of water available for dilution consists only of the shallow surface layer. Instead, it is the amount of river runoff that controls the extent to which a contaminant may be diluted. The metal depth contours (Figures 2.8, 2.9, 2.10) show clearly how the deeper waters remain unaffected by high metal loads in the creek. They also demonstrate the considerable amount of spatial variability brought about by wind- and tide-induced changes in surface circulation. The work of Buckley (1977) shows that circulation patterns can change dramatically on time scales of half a day or so. They are driven predominantly by wind and river discharge, while tidal forces appear to exert only a minor influence. Downchannel winds and high river runoff may cause the flow of the entire surface layer to be seaward. After a period of strong up-inlet winds, this pattern may be reversed and the Squamish River outflow may be pushed back towards the head, leading to northward surface currents. In this situation, the gravitational forces will eventually exceed the wind stress and the river outflow will

again start to move seaward. Quite frequently, there is runoff-driven outflow along the western shore that drives a counterclockwise eddy in Britannia Bay.

As it enters Britannia Bay, the creek outflow will be deflected according to the prevailing surface current. Depending on the particular conditions, it may move northwards along the shore, go straight out in a westward direction or be deflected to the south. As a result, the creek plume may be missed at either or both Stations A and B, as observed for example in December 1993 where high surface concentrations were found at the distal Station A, but not at Station B close to the mine, or in May, where the creek plume apparently bypassed both sites (Figure 2.8).

2.4.4.2. Dispersion of Submarine Discharge

The subsurface discharge of acid mine drainage via the submerged outfall is thought to rise directly to the surface during late fall and winter when the pycnocline is not very strong (Figure 2.7). Besides the absence of any deep metal signals during this time, there is observational evidence supporting this assumption. On two cruises in March 1994, a patch of lighter coloured water about 10 m across was visible intermittently close to the outfall. Attempts to track these events using a salinity/temperature recorder or by acoustic imaging were unsuccessful, for two reasons. First, the salinity and temperature signature of the discharge gets lost as it mixes with seawater (see below) so that it can only be recorded in the immediate vicinity of the outfall. Second, the volume of water discharged in the winter is small (on the order of 0.6 m^3/s), giving rise to a very local plume that may only occasionally increase in size as municipal sewage is pumped into the discharge.

During periods of strong stratification, i.e. from about March to September (Figure 2.7), the plume is expected to be trapped below the pycnocline. This was in fact observed in June, July and August where the presence of the plume was manifested by elevated Cu, Cd and Zn concentrations at or below 10 m. However, the signal was missing at other times, for two possible reasons. First, the direction of dispersion in the horizontal is not known. Generally currents below about 10 m depth are up-inlet, with changes in their magnitude induced by tides (Buckley 1977). The subsurface plume could therefore be deflected to the north and bypass the two sampling sites. Second, the bottom of the pycnocline deepens from about 3 m in March to about 11 m in June and then shoals again to about 7 m in September. If the plume is not very thick (1 m or less), it could be quite easily missed by a sampling scheme using 5 m depth intervals. The thickness of the plume may also be influenced by the intermittent admixture of municipal sewage which is pumped into the outfall pipe at irregular intervals.

Even though the signature of the subsurface discharge is not as frequently observed as expected, there is little doubt that upon mixing with seawater, acid mine drainage forms a neutrally buoyant plume that gets trapped below the pycnocline during periods of strong stratification. This is demonstrated by vertical profiles taken in August 1994 in the immediate vicinity of the outfall. The exact location of the outfall was determined previously by SCUBA-divers and marked with a float. The salinity and temperature profiles (Figure 2.26) show the usual two-layered structure, but a plume signal is notably absent, even though there is clear evidence for its presence from metal profiles (Figure 2.27). The lack of a distinct salinity and temperature signal can be explained as follows. It appears that the samples at 25 and 20 m depth were taken slightly off the plume rising from the pipe and that they represent the surrounding salt water rather than a mixture of salt water and freshwater. The samples at 15 and 10 m, which are within the plume, represent discharge that has mixed with a considerable amount of salt water, so that their
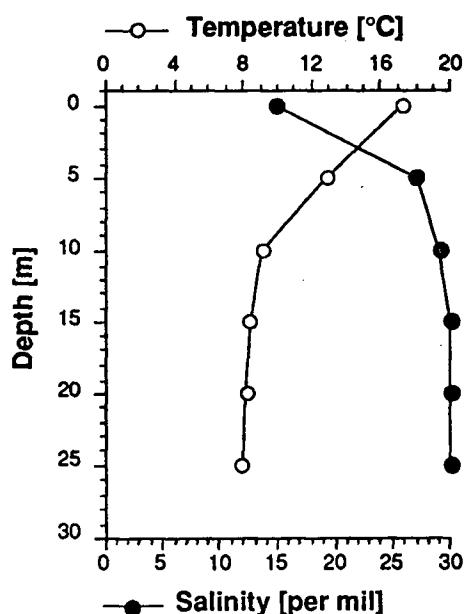
Figure 2.26. Salinity and temperature profiles in the immediate vicinity of the submarine outfall. The samples were taken in August 1994. Bottom depth is 30m.

salinity and temperature (and hence their density) are close to the surrounding water. Above the pycnocline, salinity and temperature are controlled by the characteristics of the surface layer.

Dissolved Cu, Cd and Zn profiles (Figure 2.27 a, b, c) exhibit elevated concentrations at 15 and 10 m which are evidence for the presence of the plume at these depths. The particulate metal fraction in these profiles suggests that the removal processes observed in the creek also control metal behaviour in the deep discharge. For example, the concurrent maxima of dissolved Cu and of % $Cu_{part.}$ (the fraction of total Cu present as particles) implies that there is considerable removal of Cu from the dissolved phase (Figure 2.27 a). (The high percentages of particulate metal at the surface and at depth are likely caused by removal processes in the creek mixing zone and by resuspension at the bottom, respectively). In contrast, there is very little removal of Cd and Zn as the plume mixes with salt water (Figure 2.27 b, c), which again agrees with the behaviour observed in the creek. Likewise, Fe is removed very rapidly (Figure 2.27 d), as indicated by the high part./diss. ratio and the almost straight profile of dissolved iron. (The maximum at the surface is likely a result of high concentrations in Squamish River input). Visual evidence for the extensive flocculation and precipitation of metals, particularly iron oxyhydroxides, exists in the reports of divers, who observed that upon exiting the outfall the discharge took on a milky yellow appearance (LeBlanc, pers. comm.). The percentage of metal present in particulate form at 15 m (24, 0.5, 4 and 94% for Cu, Cd, Zn and Fe, respectively) is comparable to what is usually found in the creek mixing zone. In summary, these observations suggest that there is no qualitative difference in the behaviour of dissolved Cu, Cd, Zn and Fe from acid mine drainage when discharged at depth rather than at the surface. This result was confirmed in a laboratory mixing experiment described in detail in Chapter 3.
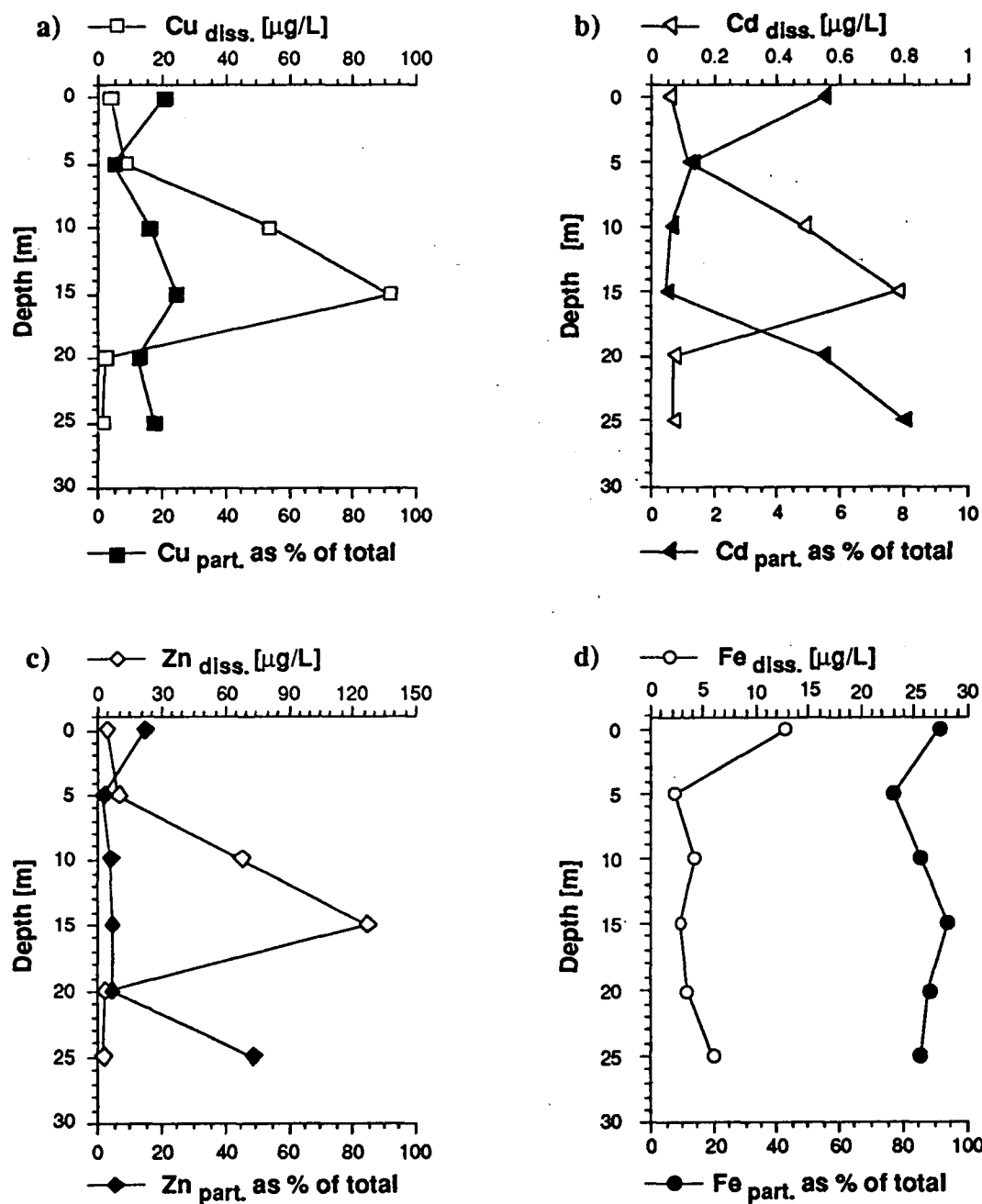
Figure 2.27. Dissolved metals (in µg/L) and particulate metals (expressed as percentage of the total) near the outfall. a) Cu, b) Cd, c) Zn, d) Fe.

2.4.5. Contaminant Dispersion Estimate Using Box Model

The surface transects and vertical profiles of metals discussed in previous sections have provided some important information relevant to assessing the fate of acid mine drainage in Howe Sound, which can be summarized as follows:

1. Dispersion of metals from Britannia Creek is within the surface layer of Howe Sound only, not with the whole body of water. Deep discharges may additionally result in elevated metal concentrations in the subsurface layer.

2. The amount of metal delivered is dependent on hydrological conditions, with peaks in winter and spring.

3. A considerable amount of Cu and small proportions of Zn and Cd are removed from solution as Britannia Creek mixes with seawater. The removal efficiency is directly related to the metal concentration in the creek.

4. Most of the Zn and Cd, and variable amounts of Cu (usually on the order of 50%) are present in dissolved form.

5. Expected metal concentrations in Britannia Bay often do not match the observations because of changes in the extent and direction of lateral advection of the creek plume by surface currents.

A more quantitative way of describing the dispersion of contaminants makes use of physical models of estuarine circulation. A simple approach uses box models to describe the circulation-driven dispersion of metals and nutrients (Bewers and Yeats 1978, Petrie and Yeats 1990, Shiller 1996). The model used here consists of two compartments representing the estuarine surface and subsurface layer. Squamish River water flows through the surface box and entrains water from the layer below, resulting in an upward flux of water. The entrained water is replaced by water from outside the lower box. The resulting volume fluxes between the boxes can be calculated from the equations for

conservation of volume and conservation of salt (see Appendix A.3.1 for graphical representation and equations). The choice of the boundaries for each box is arbitrary; the entire upper basin was chosen to represent the lateral dimensions of the boxes, primarily because of the lack of hydrographic data needed for a finer resolution, and because a large box minimized problems arising from lateral inhomogeneities due to incomplete mixing. The bottom of the pycnocline was chosen as the boundary between the upper and the lower box since in Knight Inlet, another B.C. fjord, it was found that horizontal current speeds were lowest at this depth (Pond, pers. comm.). (Theoretically, since horizontal currents move in opposite directions in the surface and subsurface layer, the current speed at their boundary should be zero.) The bottom of the lower box was determined from salinity profiles as the depth at which salinity became uniform. Input data required are river discharge, the mean salinity of the two boxes (which was calculated from salinity profiles at Station A) and the salinity of the water entering the lower box. In September, salinity measurements made at Porteau Cove were used to provide this number, while in the other instances an estimate based on the salinity of the lower box had to be made due to the inavailability of data. An underestimate of the salinity by 2‰ would lead to decreases in the volume flux out of the upper box by about 1% or 40% in the June 1994 or the January 1995 cases, respectively. Metal input was assumed to proceed via initial mixing with Squamish River before entering the surface box. An effective metal concentration that accounted for the percentage of metal that would be removed upon mixing with seawater was calculated using the removal efficiencies given in Table 2.4. Metal concentrations in Squamish River water were estimated from two field samples taken in June 1994 and 1996. The model is not very susceptible to these values since they are much smaller than the mine input. The lower box represented another source of metal, with concentrations determined from the respective metal profiles. The model was tested using three scenarios, corresponding to the three different regimes observed in the field (Table 2.5).

	May 1994	September 1994	January 1995
River runoff	high	intermediate	low
Creek runoff	high	low	low
Creek metal conc.	high	low	high

Table 2.5. Characteristics of the three seasonal scenarios investigated using a box model.

Input values and the full results are given in Appendix A.3.2, and the main findings are listed in Table 2.6. The physical data show that periods of high river discharge are characterized by high volume fluxes (Q_4) out of the surface box due to enhanced entrainment. The mean velocity of the outflow does not change much, hence the increased volume flux results entirely from the deepening of the pycnocline. The calculated velocities compare well with those calculated using a similar approach (5 and 6 cm/s, Buckley and Pond 1976) and with the long-term average from current meter measurements at 3 m depth ($\approx 3.5 \pm 1$ cm/s, Buckley 1977).

The metal concentrations in the surface outflow reflect the expected seasonal pattern, where concentrations are highest during freshet and lowest in the fall in response to metal loads in the creek and to river runoff. Also shown in Table 2.6 are the measured surface concentrations at Station A. The calculated concentrations are for a site downstream of A and are therefore not necessarily expected to match the observations at Station A; indeed, they should be lower as a result of continuing dilution as the surface outflow travels from site A to the mouth of the upper basin. Also, the calculations imply horizontally homogeneous distributions of metals, while in reality there may still be a cross-channel gradient for quite some distance downstream. Comparison with the observed metal concentrations shows, however, that the calculated seasonal trends agree with the observations. Also, despite the considerable amount of dilution during freshet, metal concentrations at the mouth of the upper basin are still high, suggesting a potential for toxic effects on surface-dwelling organisms. It will be shown in Chapter 4 that the

concentration of 8 µg/L Cu calculated for May could be high enough to adversely affect growth of endemic phytoplankton species.

	May 1994	September 1994	January 1995
Physical data			
surface outflow [m³/s]	1300	511	376
mean velocity [cm/s]	4.12	5.98	4.19
depth of upper box [m]	10.6	2.84	2.99
Calc. metal conc. in surface layer			
Cu [µg/L]	8.64	1.23	3.47
Cd [µg/L]	0.072	0.042	0.073
Zn [µg/L]	6.44	3.42	4.36
Observed metal conc. at Station A			
Cu [µg/L]	18.6	1.48	10.8
Cd [µg/L]	0.106	0.057	0.115
Zn [µg/L]	28.4	4.88	9.93
Calc. metal conc. (outfall included)			
Cu [µg/L]	11.1	3.19	8.29
Cd [µg/L]	0.093	0.064	0.102
Zn [µg/L]	11.6	6.67	10.8

Table 2.6. Modeling results for the three scenarios listed in Table 2.5. Calc. = calculated, conc. = concentration.

Acid mine drainage discharged at 30 m depth will rise to the surface during periods of weak stratification (i.e. in the January scenario), thereby increasing metal inputs to the upper box. The effect of the subsurface discharge during the remainder of the year (i.e. in the May and September cases) is difficult to assess, since it is not known whether the buoyant plume will leave the estuary in a subsurface layer or whether it will be mixed up into the surface box via entrainment. An upper limit on its effect on surface

concentrations can be obtained by allowing the subsurface discharge to mix with surface waters, which in essence amounts to the same as if it were discharged via Britannia Creek. This case was modelled by using a combined Britannia Creek/AMD end-member rather than Britannia Creek alone. Metal concentrations in the discharge were known from field measurements (Figure 2.19). There are no corresponding streamflow records from the 4100 portal available for 1994, thus they had to be extrapolated from the 1993 streamflow record (Figure 2.18) using 1994 Britannia Creek discharge data (Figure 2.16). The calculations show that under these conditions, the additional metal load raises surface Cu, Cd and Zn concentrations by up to a factor of 2. The largest increase is observed in January, where the high metal loads get considerably less diluted by freshwater than in spring due to reduced river runoff.

2.4.6. Vertical Metal Transport

To this point, only the dispersion of the dissolved metal fraction has been addressed. It is reasonable to do so in the case of Zn and Cd since they are present predominantly in the dissolved form. In contrast, Cu is associated to a significant degree with the particulate fraction, for which dispersion mechanisms may be quite different. In their study of particulate metals in a polluted Norwegian fjord, Skei and coworkers (1973) observed elevated particulate Cu, Zn and Pb concentrations in surface waters almost 10 km away from the source. This suggests that particulate metals may remain suspended for quite some time before being removed to deeper waters.

Incorporation of metals in phytoplankton hard parts and adsorption onto settling biogenic material could contribute to the vertical transport of metals. For example, Slauenwhite and Wangersky (1991) showed that after a phytoplankton bloom, the flux of particulate Cd increased, while there was little change in the flux of Cu. Attempts to demonstrate similar transport processes in the open ocean using sediment traps yielded inconclusive results (Noriki et al. 1985). Paulson and colleagues (1993) showed that in Hood Canal, a fjord-type branch of Puget Sound, Zn was taken up by phytoplankton in surface waters and released at depth through remineralization. Cd was also affected by these processes, albeit to a lesser degree, and no biological control was observed for Cu. In contrast, Windom and coworkers (1991) concluded that in the Savannah, Maeklong and Medway estuaries, biological processes did not significantly affect cycling of any of the three metals. In Howe Sound, biological controls on metal removal are not likely to be important, since productivity is low due to light scattering by the silt load in surface waters (Stockner et al. 1977). Scanning electron microscopy studies (see Chapter 3) also indicate that biogenic particles make up only a small fraction of the particulate matter load.

Evidence from sediment traps deployed in upper Howe Sound shows that sedimentation of Cu-rich particles is greater in the vicinity of the mine, both in absolute terms and relative to the detrital load. Particulate fluxes at the deepest traps (200 m at Station A, 80 m at Station B) were 1.4 and 3.6 μg Cu m^{-2} day^{-1}, respectively (Figure 2.12). The corresponding Cu/Al weight ratios were 0.001 and 0.004 at Stations A and B, respectively. The value at the distal Station A is identical to the sedimentary ratio, calculated as the mean of 23 upper-basin cores away from the mine, using Drysdale's (1990) data. This indicates that the flux at the distal site comprises mostly detrital material, while at the station close to the mine particles are significantly enriched in Cu even at depth. Ratios in suspended particles obtained from filtration of water samples are also generally higher than the sediment value, but are quite variable and do not exhibit any spatial or seasonal trends (Figure 2.28). This material seems distinctly different from the particles collected in traps. In his sediment trap study in Howe Sound, Syvitski (1978) observed a lack of correlation between sedimentation rates and turbidity of the water around sediment traps, which led him to conclude "that much of the suspended sediment in the lower marine water exists simply as background through which larger particles settle". Bottle casts are known to collect this background material preferentially, while they may miss larger, rapidly-sinking particles (Calvert and MacCartney 1979). It is likely that some Cu-rich material remains suspended and does not contribute much to the vertical particulate metal flux.

In conclusion, sedimentation of Cu-bearing particles in Britannia Bay may be significant. However, we do not have the means at present to quantify this. Outside Britannia Bay, where flocculation and sedimentation of Cu is greatly reduced, the proportion of particulate Cu exported via estuarine surface circulation may be estimated from Syvitski's (1978) data. He calculated that more than 50% of the original suspended particulate matter in the surface layer exits Howe Sound during times of high discharge. For particulate Cu, which in other estuaries is known to be present to a large extent as

fine-grained and colloidal particles (Martin et al. 1995, Muller 1996), this percentage may be significantly higher, since much of the suspended load is in the silt and clay size fractions (Syvitski 1978). It would appear then that at least 50% of the particulate Cu outside of Britannia Bay (which generally makes up about 10% of the total Cu at this site) exits upper Howe Sound with the estuarine surface circulation.
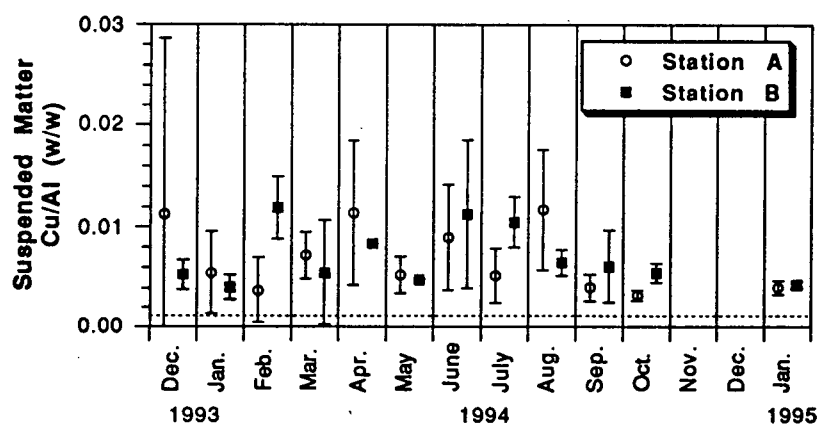
Figure 2.28. Mean particulate Cu/Al ratios in suspended particulate matter collected at Stations A and B. Error bars represent one standard deviation of four (Station A) and three samples (Station B). Only water samples at or below 30 m depth were considered. Anomalously high values in April and June possibly related to slope instabilities were omitted. The dotted line indicates background sedimentary value in Howe Sound (see text).

2.5. Conclusions

Using both dissolved and particulate metal data from a series of surface transects, the removal of Fe and Cu and the quasi-conservative nature of Cd and Zn in the mixing zone was demonstrated. The example of Cd also showed that using only dissolved rather than both dissolved and particulate metal data can lead to erroneous conclusions regarding the behaviour of metals during mixing, for instance if salinity does not provide a conservative index of mixing due to the presence of several seawater end-members. The reactant approach as described by Liss (1979) is only applicable under well-defined conditions which are often implied to be present in the natural environment, although this assumption is rarely verified. It would therefore appear that some of the evidence of conservative or non-conservative behaviour of metals reported in the literature may have to be reviewed in terms of whether or not the reactant approach is valid under the conditions encountered. In the absence of large-scale metal removal via rapidly sinking particles, the reactant approach can be validated by simultaneously measuring dissolved and particulate metal concentrations using two lines of evidence. Firstly, the proportions of the two fractions provides an estimate of the possible involvement of the particulate phase in metal removal/release processes. If metal is released during mixing, the particulate metal concentration has to decrease concurrently with increasing dissolved metal, and there has to be enough metal present in the particulate form to cause such an increase in the dissolved fraction, as observed for example in the Fraser River estuary by Fletcher et al. (1983). Secondly, in the absence of large-scale removal via rapidly-sinking particles, the total metal concentration (defined as the sum of particulate and dissolved) has to behave conservatively, if the index of mixing chosen is in fact conservative. Such conservative behaviour has been shown for total Cu, Zn and Fe in the mixing zone of Britannia Creek, using Cd as tracer for dilution.

Evidence from an extensive field study and modeling using a simple box model shows that metal dispersion in Howe Sound is strongly controlled by the physical properties of the estuary, namely its density stratification and its surface outflow. Not only are there longitudinal metal concentration gradients from increasing dilution of Britannia Creek with estuarine surface water, but there are often also strong lateral gradients. High variability of the direction of the surface currents leads to rapidly changing horizontal dispersion patterns of the creek plume. As a result, metal concentrations in surface waters in upper Howe Sound are far from being uniform. Extrapolation of average surface metal concentrations from discrete samples is not recommended if, for example, the intention is to compare them with water quality criteria, unless the samples are numerous and well distributed over the entire area.

There is considerable seasonal variability as a result of changing hydrological conditions, since the amount of metals delivered from the mine, as well as the Squamish River and Britannia Creek discharge, are determined by hydrological factors. The resulting surface metal concentrations are most likely to peak in winter and during freshet. The spring peak could be of particular concern from a toxicological point of view, since it may coincide with the spring phytoplankton bloom. Experiments were performed to address this issue and are discussed in detail in Chapter 4.

The dispersion of Cd and Zn can be adequately described by the behaviour of the dissolved fraction, while with Cu a variable, but often non-negligible proportion is associated with the particulate phase. The dispersive behaviour of particulate Cu could not be determined in quantitative terms, but it appears likely that much of it remains suspended and leaves upper Howe Sound via estuarine surface circulation in a similar fashion as the dissolved fraction.

The discharge of acid mine drainage via a submarine outfall additionally contributes dissolved and particulate metals. While during winter and early spring the discharge rises to the surface and represents in essence another surface source of metals, it remains

trapped below the pycnocline during periods of strong stratification. The ultimate fate of this neutrally buoyant plume is likely advection into the surface layer by entrainment of intermediate water, whereby it again increases surface concentrations. Estimates indicate that in this case the increase in surface metal concentrations may be as much as a factor two. It appears that there is little benefit, other than cosmetic, in discharging acid mine drainage at depth under the present scheme. One might consider using the deep waters as a repository for AMD, however. In order to prevent it from rising to the surface, the density of the discharge would have to be equal to or greater than the density of the deep water (≈ 1.03 g/cm^3), for example by premixing it with seawater and addition of salt. It goes without saying that at the same time the problem of discharging municipal sewage through the same outfall should be addressed.

The removal of metals in the estuarine mixing zone has been discussed here only as far as it is relevant for calculating effective metal concentrations in Britannia Creek. A linear relationship between the extent of metal removal and metal concentrations in the creek was found which suggests that metal removal could be controlled by precipitation processes. A more detailed investigation into these mechanisms is presented in the following chapter. Although a great deal of literature has been published on metal behaviour in estuaries, it is important to study these processes in a contaminated system because the relative importance of the governing parameters may be quite different from a more pristine environment. Also, in the long run it would be useful to make predictions on metal dispersion and behaviour, and more often than not these estimates are needed in areas impacted by anthropogenic contamination.

2.6. References

Balistrieri, L.S. and J.W. Murray, 1982. The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater. Geochim. Cosmochim. Acta **46**, 1253 - 1265.

Balistrieri, L.S. and J.W. Murray, 1984. Marine scavenging: Trace metal adsorption by interfacial sediment from MANOP site H. Geochim. Cosmochim. Acta **48**, 921 - 929.

Barton, P., 1978. The acid mine drainage. In: Sulfur in the environment, J. O. Nriagu ed., Wiley, New York, 314 - 356.

Benjamin, M.M. and J.O. Leckie, 1981a. Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J. Colloid Interf. Sci. **79**, 209 - 221.

Benjamin, M.M. and J.O. Leckie, 1981b. Competitive adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J. Coll. Interf. Sci. **83**, 410 - 418.

Benjamin, M.M. and J.O. Leckie, 1982. Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behavior of Cd on oxide surfaces. Environ. Sci. Technol. **16**, 162 -170.

Bewers, J.M. and P.A. Yeats, 1978. Trace metals in the waters of a partially mixed estuary. Estuar. Coastal Mar. Sci. **7**, 147 - 162.

Boyle, E., R. Collier, A.T. Dengler, J.M. Edmond, A.C. Ng and R.F. Stallard, 1974. On the chemical mass-balance in estuaries. Geochim. Cosmochim. Acta **38**, 1719 - 1728.

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

Brady, K.S., J.M. Bigham, W.F. Jaynes and T.J. Logan, 1986. Influence of sulfate on Fe-oxide formation: Comparisons with a stream receiving acid mine drainage. Clays and Clay Minerals **34**, 266 - 274.

Bruland, K.W. and K.H. Coale, 1985. Analysis of seawater for dissolved cadmium, copper and lead: an intercomparison of voltammetric and atomic absorption methods. Mar. Chem. **17**, 285 - 300.

Buckley, J.R. and S. Pond, 1976. Wind and the surface circulation of a fjord. J. Fish. Res. Board Can. **33**, 2265 - 2271.

Buckley, J.R., 1977. The currents, winds and tides of northern Howe Sound. Ph.D. thesis, University of British Columbia, Vancouver, B.C.

Calvert, S.E. and M.J. MacCartney, 1979. The effect of incomplete recovery of large particles from water samples on the chemical composition of oceanic particulate matter. Limnol. Oceanogr. **24**, 532 - 536.

Calvert, S.E., B.L. Cousens and M.Y.S. Soon, 1985. An X-ray fluorescence spectrometric method for the determination of major and minor elements in ferromanganese nodules. Chem. Geol. **51**, 9 - 18.

Chapman, B.M., D.R. Jones and R.F. Jung, 1983. Processes controlling metal ion attenuation in acid mine drainage streams. Geochim. Cosmochim. Acta **47**, 1957 - 1973.

Colbourne, E.B. and A.E. Hay, 1990. An acoustic remote sensing and submersible study of an Arctic submarine spring plume. J. Geophys. Res. **95**, 13219 - 13234.

Drysdale, K., 1990. Geochemistry of a buried marine mine tailings deposit, Howe Sound, B.C. M.Sc. thesis, University of British Columbia, Vancouver, B.C.

Duinker, J.C., 1980. Suspended matter in estuaries: Adsorption and desorption processes. In: Chemistry and biochemistry of estuaries, E. Olausson and I. Cato eds., Wiley-Interscience, New York, 121 - 151.

Duinker, J.C., 1983. Effects of particle size and density on the transport of metals to the ocean. In: Trace metals in seawater, C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg eds., Plenum Press, New York, 209 - 226.

Eckert, J.M. and E.R. Sholkovitz, 1976. The flocculation of iron, aluminium and humates from river water by electrolytes. Geochim. Cosmochim. Acta **40**, 847 - 848.

Flegal, A.R., G.J. Smith, G.A. Gill and S. Sanudo-Wilhelmy, 1991. Dissolved trace element cycles in the San Francisco Bay estuary. Mar. Chem. **36**, 329 - 363.

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.

Goyette, D. and K. Ferguson, 1985. Environmental assessment of the Britannia Mine - Howe Sound. Department of the Environment, Environmental Protection Service Pacific Region, Vancouver, B.C.

Hong, H. and D.R. Kester, 1985. Chemical forms of iron in the Connecticut River estuary. Estuar. Coastal Shelf Sci. **21**, 449 - 459.

Johnson, C.A. and I. Thornton, 1987. Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. Water Res. **21**, 359 - 365.

Karlsson, S., P. Sandén and B. Allard, 1987. Environmental impacts of an old mine tailings deposit - metal adsorption by particulate matter. Nordic Hydrol. **18**, 313 - 324.

Knauer, G.A., D.M. Karl, J.H. Martin and C.N. Hunter, 1984. *In situ* effects of selected preservatives on total carbon, nitrogen and metals collected in sediment traps. J. Mar. Res. **42**, 445 - 462.

Krone, R.B., 1978. Aggregation of suspended particles in estuaries. In: Estuarine Transport Processes, B. Kjerfve ed., University of Southern California Press, Davis, 177 - 190.

Li, Y.-H., L. Burkhardt and H. Teraoka, 1984. Desorption and coagulation of trace elements during estuarine mixing. Geochim. Cosmochim. Acta **48**, 1879 - 1884.

Liss, P.S., 1976. Conservative and non-conservative behaviour of dissolved constituents during estuarine mixing. In: Estuarine chemistry, J. D. Burton and P. S. Liss eds., Academic Press, London, 93 - 129.

Loder, T.C. and R.P. Reichard, 1981. The dynamics of conservative mixing in estuaries. Estuaries 4, 64 - 69.

Martin, J.-M., M.-H. Dai and G. Cauvet, 1995. Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). Limnol. Oceanogr. 40, 119 - 131.

Morton, B.R., 1959. Forced plumes. J. Fluid Mech. 5, 151 - 163.

Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. Mar. Chem. 52, 245 - 268.

Muller, F.L.L., P.W. Balls and M. Tranter, 1996. Annual geochemical mass balances in waters of the Firth of Clyde. Oceanol. Acta 18, 511-521.

Noriki, S., N. Ishimori, K. Harada and S. Tsunogai, 1985. Removal of trace metals from seawater during a phytoplankton bloom as studied with sediment traps in Funka Bay, Japan. Mar. Chem. 17, 75 - 89.

Officer, C.B., 1979. Discussion of the behaviour of nonconservative dissolved constituents in estuaries. Estuar. Coastal Mar. Sci. 9, 91 - 94.

Parsons, T.R., Y. Maita and C.M. Lalli, 1989. A manual of chemical and biological methods for seawater analysis. 2nd ed., Pergamon, Oxford, 101 - 109.

Paulson, A.J., 1986. Effects of flow rate and pretreatment on the extraction of trace metals from estuarine and coastal seawater by Chelex-100. Anal. Chem. 58, 183 - 187.

Paulson, A.J., R.A. Feely, H.C. Curl Jr., E.A. Crecelius and T. Geiselman, 1988. The impact of scavenging on trace metal budgets in Puget Sound. Geochim. Cosmochim. Acta 52, 1765 - 1779.

Paulson, A.J., H.C. Curl Jr. and R.A. Feely, 1993. The biogeochemistry of nutrients and trace metals in Hood Canal, a Puget Sound fjord. Mar. Chem. 43, 157 - 173.

Pavlova, V. and L. Sigg, 1988. Adsorption of trace metals on aluminium oxide: a simulation of processes in freshwater systems by close approximation to natural conditions. Water Res. 22, 1571 - 1575.

Petrie, B. and P. Yeats, 1990. Simple models of the circulation, dissolved metals, suspended solids and nutrients in Halifax Harbour. Water Poll. Res. J. Canada 25, 325 - 349.

Price, W.A., T. Schwab and N. Hutt, 1995. A reconnaissance study of acid mine drainage at the Britannia mine. B.C. Ministry of Energy, Mines and Petroleum Resources, Victoria, B.C.

Robertson, E., 1990. Monitoring acid mine drainage. B.C. Acid Mine Drainage Task Force, Vancouver, B.C.

Salomons, W. and H. Förstner, 1984. Metals in the hydrocycle. Springer, Berlin.

Scanes, P.R. and N. Philip, 1995. Environmental impact of deepwater discharge of sewage effluent off Sidney, NSW, Australia. Mar. Poll. Bull. **31**, 343 - 346.

Sharp, J.H., C.H. Culberson and T.M. Church, 1982. The chemistry of the Delaware estuary: general considerations. Limnol. Oceanogr. **27**, 1015 - 1028.

Shiller, A.M., 1996. The effect of recycling traps and upwelling on estuarine chemical flux estimates. Geochim. Cosmochim. Acta **60**, 3177 - 3185.

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

Sholkovitz, E.R. and D. Copland, 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. Geochim. Cosmochim. Acta **45**, 181 - 189.

Skei, J.M., N.B. Price and S.E. Calvert, 1973. Particulate metals in waters of Sörfjord West Norway. Ambio **2**, 122 - 124.

Slauenwhite, D.E. and P.J. Wangersky, 1991. Behaviour of copper and cadmium during a phytoplankton bloom: a mesocosm experiment. Mar. Chem. **32**, 37 - 50.

Steffen, Robertson and Kirsten, 1991. Evaluation of ARD from Britannia Mine and the options for long term remediation of the impact on Howe Sound. Steffen, Robertson and Kirsten (B.C.) Inc., Vancouver.

Stockner, J.G., D.D. Cliff and D.B. Buchanan, 1977. Phytoplankton production and distribution in Howe Sound, British Columbia: A coastal marine embayment-fjord under stress. J. Fish. Res. Board Can. **34**, 907 - 917.

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, 43 - 87.

Stumm, W.S. and J.J. Morgan, 1996. Aquatic Chemistry. 3rd ed., Wiley, New York.

Sullivan, P.J., J.L. Yelton and K.J. Reddy, 1988. Iron sulfide oxidation and the chemistry of acid generation. Env. Geol. Water Sci. **11**, 289 - 295.

Suzuki, Y., E. Tanoue and H. Ito, 1992. A high-temperature catalytic oxidation method for the determination of dissolved organic carbon in seawater: analysis and improvement. Deep-Sea Res. **39**, 185 - 198.

Syvitski, J.P.M., 1978. Sedimentological advances concerning the flocculation and zooplankton pelletization of suspended sediment in Howe Sound, B.C., a fjord receiving glacial meltwater. Ph.D. thesis, UBC, Vancouver, B.C.

Syvitski, J.P.M. and R.D. Macdonald, 1982. Sediment character and provenance in a complex fjord; Howe Sound, British Columbia. Can. J. Earth Sci. **19**, 1025 - 1044.

Tessier, A., D. Fortin, N. Belzile, R.R. DeVitre and G.G. Leppard, 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements. Geochim. Cosmochim. Acta **60**, 387 - 404.

Walling, D.E. and I.D.L. Foster, 1975. Variations in the natural chemical concentration of river water during flood flows, and the lag effect: some further comments. J. Hydrol. **26**, 237 - 244.

Windom, H., J. Byrd, J. R Smith, M. Hungspreugs, S. Dharmvanij, W. Thumtrakul and P. Yeats, 1991. Trace metal-nutrient relationships in estuaries. Mar. Chem. **32**, 177 - 194.

CHAPTER 3

PROCESSES CONTROLLING
METAL REMOVAL
IN THE CREEK MIXING ZONE

3.1. Introduction

It was shown in the previous chapter that Cu, Cd, Zn and Fe in the mixing zone of Britannia Creek vary in their extent of non-conservative behaviour. Iron exhibited rapid and extensive removal, Cu was also removed, but to a lesser degree, while Zn and Cd behaved almost conservatively. The extent of non-conservative behaviour was observed to change from month to month, and some of this variability was attributed to the hydrological regime of Britannia Creek. In this chapter, we will investigate the controls on metal removal and how their influence changes seasonally.

The behaviour of trace metals upon mixing with seawater in estuaries has been shown to vary widely. Conservative behaviour, removal and release patterns have all been reported for Cu, Cd and Zn, while Fe appears to be removed consistently (Table 3.1). This led Bewers and Yeats to conclude in 1981 that "except for Fe and Mn, the general understanding of trace metal behaviour in estuaries is rudimentary. (...) There is insufficient information to determine any systematic behaviour of the other [trace] metals."

Fifteen years later, we have a better understanding of the underlying processes thanks to the fundamental laboratory experiments of Sholkovitz, Benjamin and Leckie and others. The interpretation of metal behaviour in natural systems, however, is more difficult because of the multitude of parameters involved. We are still unable to predict metal behaviour confidently based on a few key variables such as pH, organic matter content and concentration of dissolved iron. Moreover, in contaminated systems, which are often of particular interest due to possible impacts of anthropogenic waste discharges on the marine environment, the controlling processes and their relative importance may differ from those in a more pristine situation.

Estuary	Cu			Cd			Zn			Fe			Ref.
	con	rem	rel	con	rem	rel	con	rem	rel	con	rem	rel	
Rhone	X				X	X							1
Changjiang	X					X							2
Amazon	X					X					X		3, 4
Mississippi	X					X							5
Venice		X			X						X		6
San Fran-cisco Bay			X			X			X	X	X		7, 8
Delaware	X	X		X							X		9, 10
Scheldt			X			X			X		X		11, 12
Medway	X			X				X			X		13
Savannah			X			X			X		X		13
Maeklong	X					X	X				X		13
Tamar		X	X						X				14
Rhine		X			X						X		15
Puget Sound		X					X						16
St. Lawrence		X		X			X				X		17
Connecticut											X		18
Carnon R.		X					X				X		19
Fraser			X						X			X	20, 21

1   Elbaz-Poulichet et al. 1996
2   Edmond et al. 1985
3   Boyle et al. 1982
4   Sholkovitz et al. 1978
5   Shiller and Boyle 1991
6   Martin et al. 1995
7   Flegal et al. 1991
8   Sañudo-Wilhelmy et al. 1996
9   Sharp et al. 1982
10   Fox and Wofsy 1983

11   Salomons and Förstner 1984
12   Kerdijk and Salomons 1981
13   Windom et al. 1991
14   Morris et al. 1978
15   Duinker 1983
16   Feely et al. 1983
17   Bewers and Yeats 1978
18   Hong and Kester 1985
19   Johnson 1986
20   Thomas and Grill 1977
21   Fletcher et al. 1983

Table 3.1. Observed behaviour of metals upon mixing in various estuaries. Cons = conservative, rem = removed, rel = released.

Metal release is often observed in association with resuspension of bottom sediment in shallow and well-mixed estuaries (e.g. Bewers and Yeats 1978, Salomons and Förstner 1984, Windom et al. 1991). In the Fraser River estuary, metals desorb from riverborne particles in the mixing zone during freshet (Thomas and Grill 1977, Fletcher et al. 1983). Release from particles has been demonstrated experimentally by Li et al. (1984) and is thought to be the result of ion exchange processes at the particle surface (Duinker 1980). It is often difficult to demonstrate metal release conclusively from dissolved metal distributions due to artifacts caused by the resuspension of colloidal metal-bearing fractions or by metal inputs from of a third end-member. No evidence for large-scale release during mixing has been found in the present study.

The removal of metals may proceed via several mechanisms. Adsorptive processes (the binding of metals to particle surfaces through chemical bonds) have been intensively studied. Possibly also of significance, but much less well described are other phenomena such as precipitation (formation of insoluble metal species such as oxides and carbonates), coprecipitation (precipitation of mixed metal phases, e.g. iron-copper hydroxides) and coagulation of colloids. Since the precise mechanism of metal removal is often not known, some researchers use "flocculation" as a collective term for removal caused by adsorption, precipitation or coagulation (Sholkovitz 1976). In its specific sense, flocculation refers to the bridging of particles via chemical bonds, in contrast to aggregation, which denotes bridging via electrostatic forces (Manahan 1991). In the following, flocculation will be used in its more general sense.

The current view of metal removal in the estuarine mixing zone emphasizes adsorptive processes, whereby metals are adsorbed onto particles of either authigenic or terrigenous origin and are transported to the sediments as the particles settle out. Adsorption of trace metals can take place on the surfaces of particles such as goethite (α-Fe_2O_3, Balistrieri and Murray 1982), $Al(OH)_3$ (Pavlova and Sigg 1988), amorphous iron oxyhydroxide (Davis and Leckie 1978, Benjamin and Leckie 1981a and 1981b), estuarine

sediments (Adediran and Kramer 1987), marine sediments (Balistrieri and Murray 1984), calcite (Bilinski et al. 1991), aluminosilicates (Eliott and Huang 1981), and on organic surface coatings. Even though adsorptive processes also occur in freshwater systems, they are more important in estuaries for several reasons:

1) The salinity gradient drives the aggregation of colloid-sized particles such as iron oxyhydroxides, aluminium hydroxides and aluminosilicates. This may be a result of electrostatic interactions affecting the particles directly as described for clays (Krone 1978) or via bridging through coatings of organic matter (Manahan 1991). Aggregation leads to the removal of metals associated with colloids. The importance of colloidal material in metal transport processes has long been recognized (e.g. Sholkovitz and Copland 1981, Hunter 1983, Honeyman and Santschi 1989), and there is now growing evidence that a substantial proportion of the so-called dissolved metal pool is actually present as colloidal suspension (Martin et al. 1995, Dai and Martin 1995, Hill and Aplin 1996, Muller 1996, Sañudo-Wilhelmy et al. 1996).

2) Humic acids have been reported to flocculate upon mixing with seawater (Sholkovitz 1976, Eckert and Sholkovitz 1976, Sholkovitz et al. 1978). Since they also represent strong chelators for some metals (Buffle 1988), one would expect a loss of metal from solution associated with the removal of humic substances.

3) Specific interactions of seawater anions and cations with surface binding sites may result in increased removal of metals (Adediran and Kramer 1987, Balistrieri and Murray 1982, Sholkovitz and Copland 1981). This could occur through compression of the electrical double layer by cations, or through displacement of surface hydroxyls by doubly charged anions such as sulfate, resulting in a higher negative surface charge. The extent of adsorption will depend on the particular conditions, and in some cases no increase relative to model systems has been observed (Millward and Moore 1982, Swallow et al. 1980). The presence of

seawater can also lead to decreased adsorption as in the case of Cd, which competes with Mg for surfacebinding sites (Balistrieri and Murray 1982).

4) The increase in salinity across the estuarine mixing zone is often associated with a pH-rise. Studies with iron oxyhydroxides (Benjamin and Leckie 1981a and 1981b) and aluminium hydroxide (Pavlova and Sigg 1988) have shown that metal adsorption increases dramatically over a very narrow pH range. This so-called adsorption edge often occurs at a pH between 5 and 7, depending on the metal and the particular conditions.

Particles in natural waters are often coated with organic matter with which metals may also interact (Stumm and Morgan 1996). These coatings may enhance metal removal by favouring aggregation, since they can reduce the negative surface charge and provide the opportunity for interparticle bridging (Hunter and Liss 1982). In addition, metal removal may occur via the flocculation of humic compounds, as mentioned earlier.

In this chapter it will be shown that in addition to adsorption and complexation by flocculating organic matter, the removal of metals (specifically Cu) in the mixing zone of Britannia Creek is governed to a large extent by chemical precipitation, a processes which is generally thought to be of little importance in less contaminated estuaries. Using evidence from a one-year set of monthly field observations and from laboratory mixing experiments, the causes for the differing behaviours of Cu, Cd and Zn during mixing will be elucidated.

3.2. Methods

3.2.1. Dissolved and Particulate Metals in Field Samples

Water samples along a surface transect off Britannia Creek were collected at monthly intervals. Additionally, a set of water samples in Britannia Creek and its tributaries (the 2200 portal drainage and Jane creek) were collected in February 1996. The samples were analyzed for dissolved and particulate metals, pH, chlorophyll a, dissolved oxygen, temperature, salinity, and occasionally DOC using the methods described in Chapter 2. Dissolved sulphate in the February 1996 samples was measured on a DX-100 ion chromatograph (Dionex Corp., Sunnyvale CA) calibrated with standards of potassium sulphate in 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate.

3.2.2. Mixing Experiments

Water was collected in acid-cleaned 25 L polyethylene carboys, directly from shore in Britannia Creek and using a GOFlo bottle from a workboat at Station A in Howe Sound. In June 1996, the surface salinity at this site was only a few per mil. In order to obtain a larger salinity gradient, a 1:1 mixture was made up from surface water collected at Lions Bay (49° 27.30' N, 123° 14.30' W, salinity 14.8‰) and at Darrell Bay (49° 40.10' N, 123° 10.10' W, salinity 2.7‰). In addition, samples of 4100 portal water and of sewage were collected. The water was brought back to the lab, and a portion of it was immediately passed through 0.4 μm polycarbonate filters. The mixing experiments were performed in a similar fashion as those described by Sholkovitz (1978) using trace metal clean techniques. Weighed aliquots of filtered or unfiltered water, as appropriate, were mixed in 1 L acid-cleaned polyethylene bottles. These 1 L-samples were shaken

immediately prior to weighing, upon mixing, after about 15 minutes and again after 30 minutes, just before filtration. In each experiment, samples of filtered (or unfiltered, as appropriate) seawater and creek water were subjected to the same procedure and then filtered. Acid-cleaned 0.4 μm polycarbonate membranes were used for filtration. These were then dried and analyzed for particulate Cu, Cd, Zn, Fe and Al using microwave digestion and detection by ICP-MS and GFAAS, as described in Chapter 2. Filter balnks were negligible. Concentrations (μg/kg) were converted into volume units based on their density as inferred from salinity. Aliquots of selected samples were withdrawn for analysis of DOC, TPC, pH or dissolved metals using the methods and equipment described in Chapter 2. TPC was determined on combusted glass fibre filters (Whatman GF/F, 400°C, 4 h) using a Carlo Erba model 1500 carbon/nitrogen analyzer (Carlo Erba Strumentazione S.p.A., Milano, Italy) after the method described by Verardo et al. (1990).

3.3.3. Scanning Electron Microscopy

Imaging of particulate matter on approximately 1 cm^2 pieces of carbon coated polycarbonate filters was performed on a Philips XL30 scanning electron microscope (Philips Electron Optics, Eindhoven, Netherlands) at the departmental SEM facility. Secondary electron or back scatter electron detectors were used, as appropriate. Qualitative information on the composition of discrete particles or the entire field of view was obtained using an energy dispersive X-ray spectrometer with thin-window detector and an IMIX 4 data acquisition and analysis system (Princeton Gamma-Tech Inc., Princeton NJ).

3.3. Results

3.3.1. Mixing Experiments

3.3.1.1. Comparison between Seasons

Mixing experiments were conducted in January 1996, during a period of lower metal concentrations in Britannia Creek, and in June 1996, when metal levels were high (Table 3.2). In both experiments, filtered creek water and seawater were mixed and the flocculants produced were collected after 30 minutes. As shown in Figures 3.1 and 3.2, during both times an increase in particulate Cu and Zn concentrations at intermediate salinity can be observed, indicative of removal. In June, this was also observed with Cd, while in January particulate Cd was below detection (< 0.002 $\mu g/L$). The extent of removal (Cu > Zn > Cd) is in line with the field observations (see Chapter 2). Maximum particulate metal concentrations in spring exceeded those in January by about 80 and 30 times for Cu and Zn, respectively. This again agrees with field data, which showed that metal flocculation was more extensive when creek metal concentrations were high.

January 1996
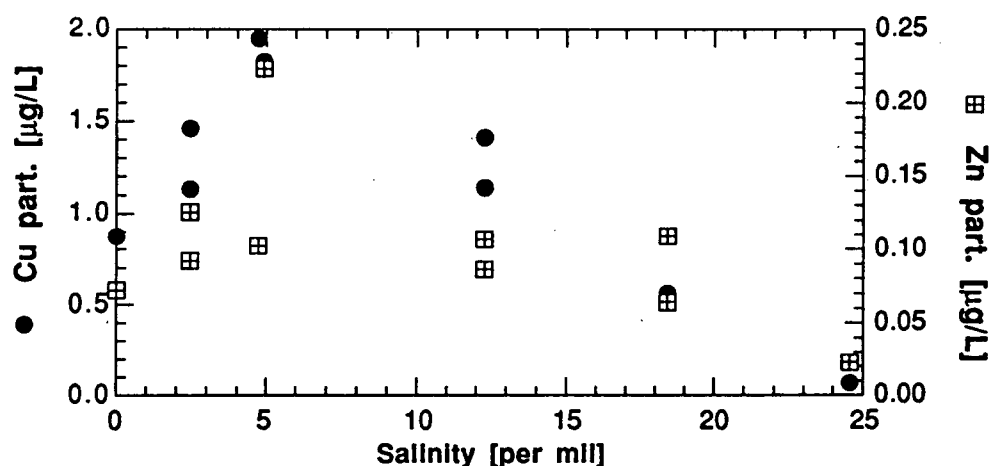
Figure 3.1. Concentrations of particulate Cu and Zn produced upon mixing of filtered creek water with filtered seawater in experiments performed in January 1996. The values are expressed as μg of particulate metal per volume of mixture. Cd was below detection (< 0.002 μg/L).
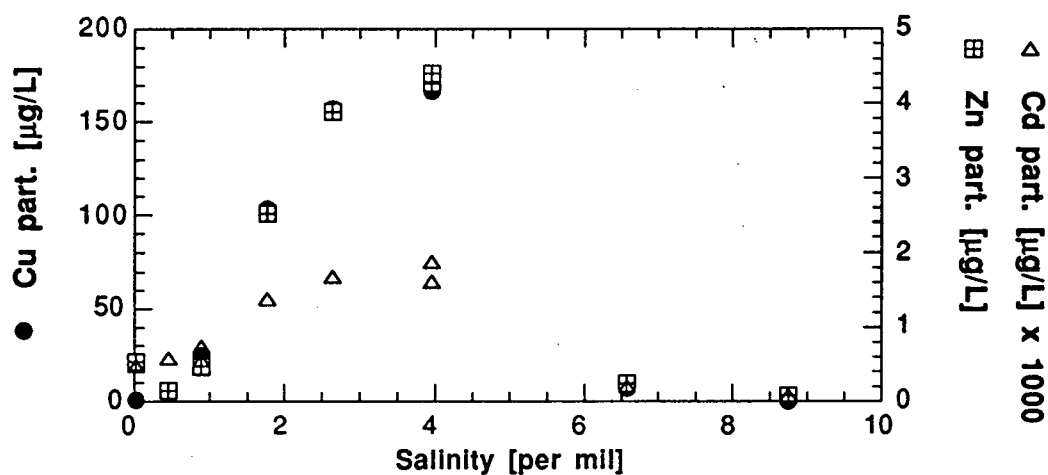
June 1996

Figure 3.2. Concentrations of particulate Cu and Zn produced upon mixing of filtered creek water with filtered seawater in experiments performed in June 1996. The values are expressed as μg of particulate metal per volume of mixture. Note that Cd concentrations are multiplied by 1000.

	January 1996		June 1996	
	Creek	Howe Sound	Creek	Howe Sound
pH	6.40	7.83	6.53	7.91
Salinity [‰]	0	24.56	0	8.75
DOC [mg C/L]	1.2	1.3	0.91	2.0
Cu [μg/L]	450	5.0	1530	2.7
Cd [μg/L]	< 0.002	< 0.002	3.0	0.022
Zn [μg/L]	350	3	560	16
Fe [μg/L]	21	27	93	7.6

Table 3.2. Dissolved metal concentrations, pH, salinity and DOC of the two end-members used in the mixing experiments shown in Figures 3.1 and 3.2.

3.3.1.2. Effects of Particles on Metal Removal

The removal of metals in the mixing zone may be enhanced by adsorption onto particle surfaces such as iron oxyhydroxides (Balistrieri and Murray 1982) or aluminosilicates (Eliott and Huang 1981). Substantial amounts of glacially-derived clays are fed into Howe Sound during freshet, which is reflected by a milky appearance of the surface waters and by elevated particulate aluminium concentrations (see Chapter 2). Mixing experiments were performed with filtered and unfiltered creek water and seawater to investigate the effect of different particle pools on metal removal.

Figure 3.3 shows that the relative amounts of Cu, Cd and Zn collected on filters are greater when particles are present. This implies that adsorptive processes do play a certain role in determining the extent of metal removal. However, even in the absence of particles in both end-members, there is still extensive removal which can not be attributed to adsorptive processes onto pre-existing particles, but has to be caused by other
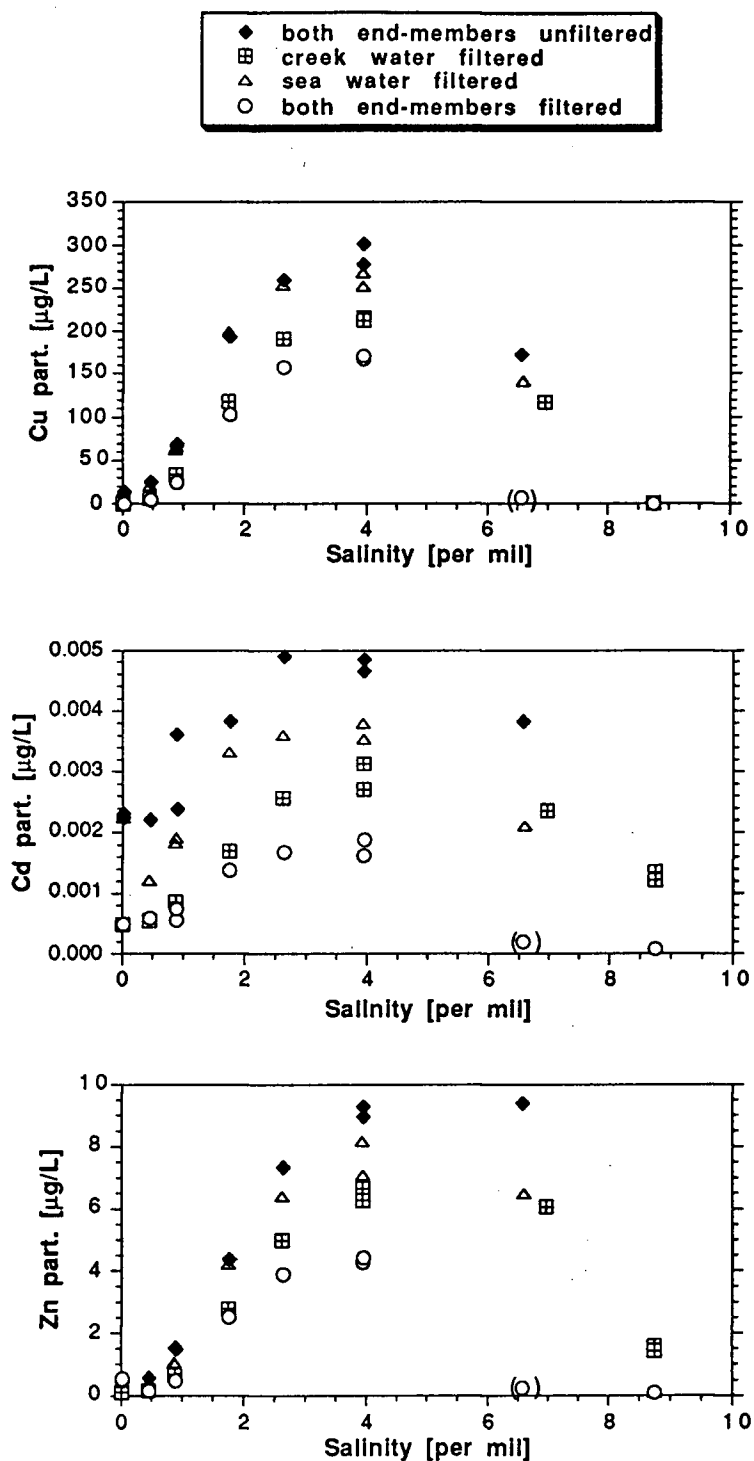
Figure 3.3. Influence of particles on the removal of Cu (top), Cd (center) and Zn (bottom) in mixtures of Britannia Creek water and seawater collected in June 1996. The concentrations are expressed as μg of particulate metal per volume of mixture. The values in brackets are inconsistent with the general trend, however we have no evidence to dismiss them as erroneous.

mechanisms such as precipitation of insoluble phases (e.g. oxides and hydroxides), adsorption of metals onto precipitates, and aggregation of colloidal particles.

3.3.1.3. Kinetics of Metal Removal

The estuarine mixing zone of Britannia Creek is fairly short. A few hundred metres off the mouth, surface salinities are almost indistinguishable from values found further away from the creek, corresponding to a probable mixing time of less than an hour. Consequently, kinetic effects (as well as salinity and pH) could have a bearing on where in the mixing zone metal removal occurs.

This question was addressed in another mixing experiment, where a portion of the water collected in January 1996 was used to produce a series of 1:1 mixtures of fresh and seawater. The flocculants produced were collected on filters as above, but at different time intervals. The experiment was repeated with the same batch of water stored cool and dark for a week before mixing. Removal of metals in the two experiments was similar (Figure 3.4), indicating that aging of the water in this fashion before mixing did not have a pronounced effect.

The amount of particulate Cu and Zn produced was fairly constant between 1 and about 30 minutes after mixing (Figure 3.4), indicating that flocculation of metals is a rapid process. However, over time scales of 2 hours or more, there was additional flocculation. Cu increased about six-fold relative to the value at less than two hours, while with Zn, there was only a three-fold increase. The scatter in the Fe data does not permit to determine conclusively whether such processes also occur with this metal.

The removal of Cu and Zn appears to occur in two stages. After initial rapid flocculation, which in the field is likely to take place in the immediate vicinity of the mouth of Britannia Creek, there is a second stage, where an additional portion of metal
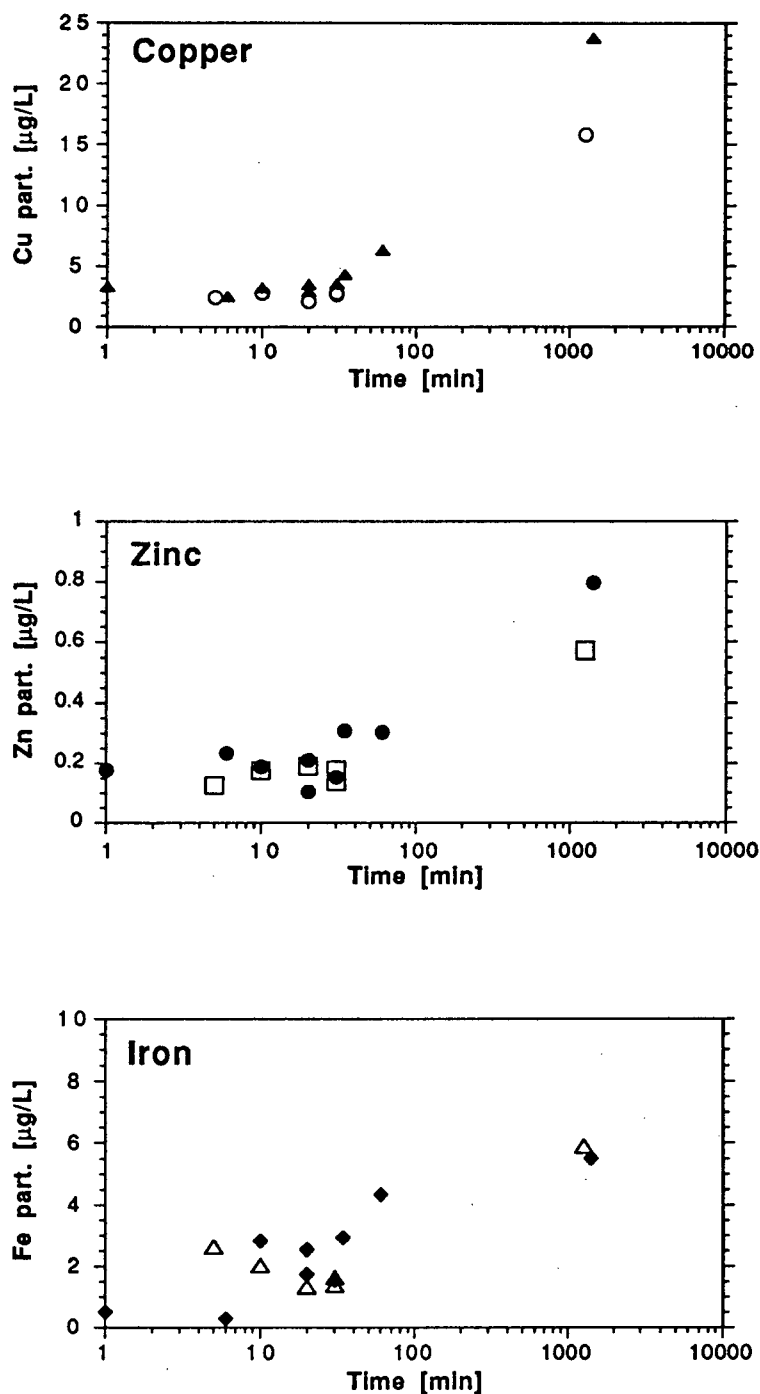
Figure 3.4. Kinetics of flocculation of Cu (top), Zn (center) and Fe (bottom) in mixtures of filtered Britannia Creek water and filtered seawater. The first experiment (open symbols) was performed within a few hours of collection, while the second (closed symbols) was done using the same water after a week of cold storage. End-members are identical to those in Figure 3.1.

flocculates, corresponding to slow removal in the surface waters of upper Howe Sound. This latter process could reflect slow kinetics of metal precipitation or colloid aggregation. The results imply that the particulate metal concentrations reported for field surface transects in this work are likely to include some fraction of the slowly flocculating metal, since the time lapse between collection and filtration of field samples was always longer than 30 minutes.

3.3.1.4. Presence of Colloidal Cu, Zn and Fe

An experiment using 0.1 and 0.4 μm pore size filters in parallel was performed to determine if there were measurable concentrations of colloidal metals. Colloids, commonly defined as particles smaller than 0.4 μm, may include metals in such various forms as crystalline precipitates, organic complexes or fine-grained weathering products of rocks. As shown in Figure 3.5, a sizable amount of Cu, Zn and Fe is present in colloidal suspension in the mixing experiment and likely also in the field, and concentrations of 0.1 μm-particulate Cu, Zn and Fe exceed those retained by 0.4 μm filters by about ten, three and two times, respectively. Most of the particulate material retained by the smaller pore size filters is produced upon mixing rather than being present in the creek end-member.

The presence of colloidal material leads to an underestimate of the particulate and an overestimate of the dissolved metal pool. The error is difficult to assess, since an unknown amount is present as particles smaller than 0.1 μm. Metal in colloidal form could also be responsible for the behaviour observed in the kinetics experiments discussed above. The amount of metal flocculating after longer reaction times was found to increase in the order Fe < Zn < Cu, which mirrors the increase in particulate metal in the < 0.4 μm fraction relative to the > 0.4 μm fraction (Figure 3.5).
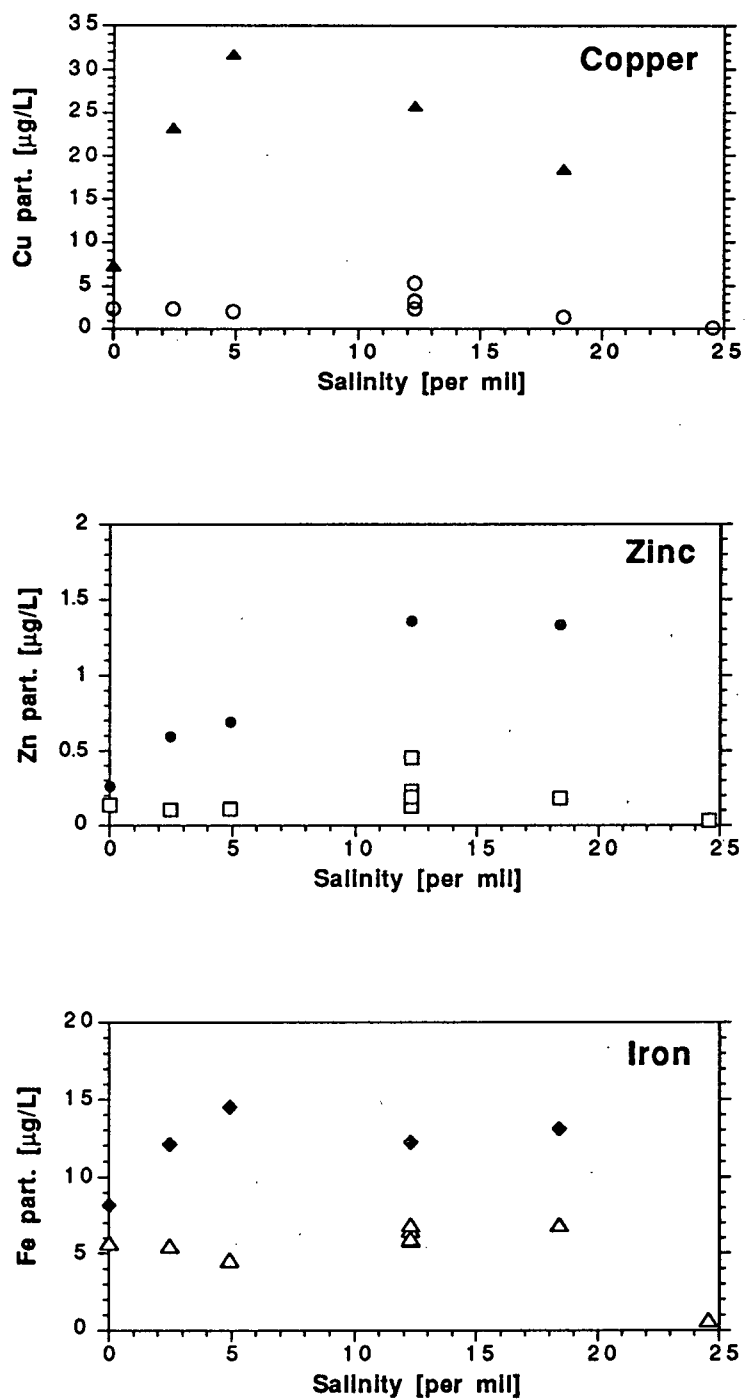
Figure 3.5. Retention of particulate Cu (top), Zn (center) and Fe (bottom) produced upon mixing of filtered Britannia Creek water and seawater by 0.4 μm (open symbols) and 0.1 μm (closed symbols) nominal pore size filter membranes. The concentrations are expressed as μg of particulate metal per volume of mixture. End-members are identical to those in Figure 3.1.

The additional Fe, Cu and Zn collected on 0.1 μm filters corresponds to > 95%, 5% and 1% of the total dissolved fraction, respectively. These values are similar to removal percentages reported for San Francisco Bay (> 85%, 16 - 20%, < 3%, respectively) by Sañudo-Wilhelmy et al. (1996). Given the different nature of the two estuaries with respect to parameters such as concentration of metals, DOC and suspended particles, the similarity is unexpected. It does agree, however, with the suggestion of the above authors that the tendency of a metal to form colloidal particles is a function of the metal itself, which can be related in part to the Irving-Williams series. This is supported by the fact that the stability of metal-humic complexes also follows the Irving-Williams series (Sholkovitz 1978).

3.3.1.5. Behaviour of Acid Mine Drainage upon Mixing and Effect of Sewage

Acid mine drainage is discharged to Howe Sound not only via Britannia Creek, but also via a subsurface marine outfall. Sewage from the Britannia Beach community is pumped into the ocean in irregular intervals via the same outfall. This experiment simulated the removal of Cu, Cd and Zn in the subsurface discharge in the presence of domestic sewage.

As shown in Figure 3.6, there is not a large difference in particulate metal concentrations at low salinity between creek and acid mine drainage, despite the considerable differences in their dissolved metal content (Table 3.3). At higher salinity, enhanced removal of metals from AMD is observed. In contrast, extensive removal even at zero salinity is apparent when sewage is added. The onset of metal removal coincides with a rise in pH to > 6.5. This value is reached upon mixing of equal parts of AMD with sewage, while in the absence of sewage a one to three mixture of AMD and seawater of 8.75‰ (resulting in a salinity of 6.6‰) is needed. Apparently, the neutralizing capacity

of sewage greatly exceeds that of seawater and leads to extensive metal removal even in the absence of sea salts. The increase in salinity upon dilution of the AMD/sewage mixture with seawater leads to additional, but much less pronounced removal (Figure 3.6).

Metal	Britannia Creek	Acid mine drainage	Sewage	AMD/sewage mixture
Cu	1530	9810	110	2570
Cd	3.0	81	1.1	44
Zn	560	18600	26	6530
Fe	93	46	180	62
Al	620	12100	140	1700

Table 3.3. Concentrations of dissolved metals (in μg/L) in freshwater end-members used in mixing experiments. In the filtered mixture (equal volumes of AMD and sewage), concentrations of Cu, Zn, Fe and Al are lower than the mean of the two sources (4960, 9315, 114 and 6114 μg/L, respectively), indicating removal of these elements upon initial mixing.
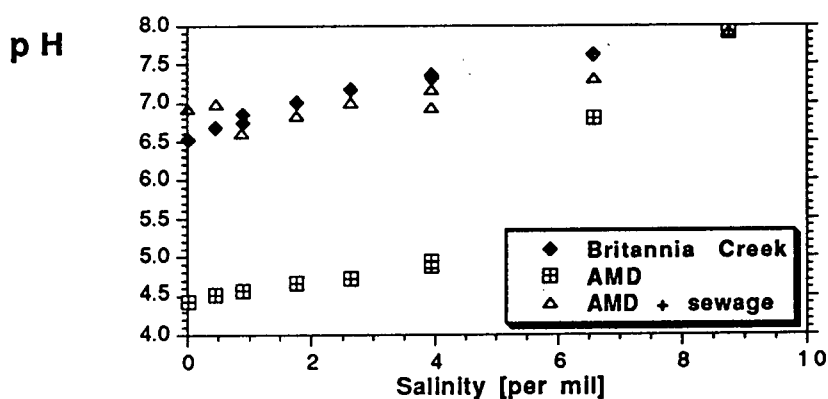
Figure 3.6 (continued next page).
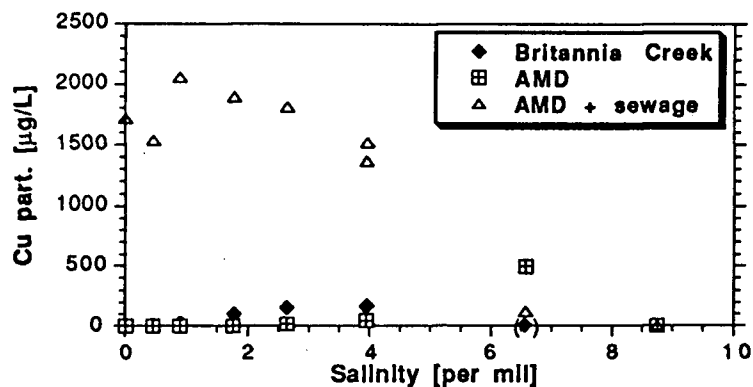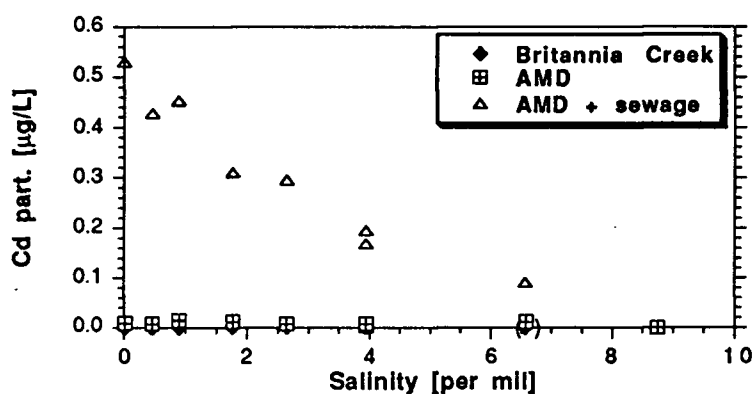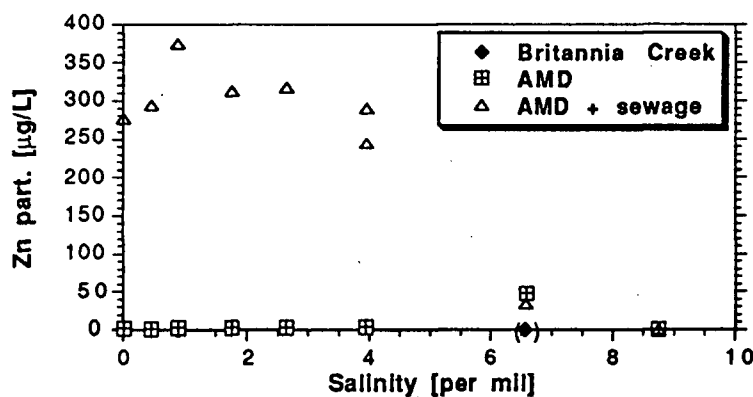
Figure 3.6 (continued). Particulate Cu, Cd and Zn concentrations (in μg/L mixture) and pH in mixing experiments where filtered Britannia Creek, acid mine drainage (AMD) or an 1:1 mixture of AMD and sewage were used as the freshwater end-members. The high starting value in the sewage experiment results from the immediate precipitation of metals upon mixing of filtered sewage and filtered AMD. This sample was not refiltered before mixing with seawater. Note that the initial dissolved metal concentration in the AMD/sewage mixture is about half of the filtered AMD. The brackets apply to the Britannia Creek experiment only and denote abnormally low values.

3.3.2. Metal Behaviour in Britannia Creek

Dissolved Fe concentrations in Britannia Creek are surprisingly low compared to Cu and Zn, bearing in mind that these metals derive from the dissolution of pyritic ores. Substantial amounts of Fe precipitate in Britannia Creek, as is evident from extensive yellow staining of the creek bed. To investigate this process further and also to explore possible associations between Cu, Zn and iron oxyhydroxides, the mixing of acid mine drainage with Britannia Creek water was monitored in the field. The sampling sites (shown in Figure 3.7) included the creek before and after input of acid mine drainage as well as the entrance to the 2200 portal, the main source of AMD to Britannia Creek.

Downstream of the 2200 portal, several small, relatively clean tributaries enter Britannia Creek and lead to dilution of the acid mine drainage (Price et al. 1995). The bouldery creek bed precluded accurate discharge measurements. In order to still be able to account for dilution effects by tributaries, a conservative tracer of acid mine drainage was needed. In an approach similar to that introduced in the previous chapter, Zn and Cd were used for this purpose. They made excellent tracers for acid mine drainage since they were present almost exclusively in dissolved form in all samples (Table 3.4) and since their only major source is the 2200 drainage.

Dissolved sulphate was found to behave non-conservatively, possibly as a result of formation of solid phases such as schwertmannite ($Fe_8O_8(OH)_6SO_4$) and jarosite ($KFe_3(SO_4)_2(OH)_6$). The presence of such sulphate minerals in acid streams has been demonstrated by Bladh (1984) and Bigham et al. (1996). Sulphate has been used as a conservative tracer of mixing in mine environments (Chapman et al. 1983), which is justified in situations where the concentration of sulphate greatly exceeds the concentration of Fe and Al. In many instances, other tracers such as Cd or Zn may be better suited.
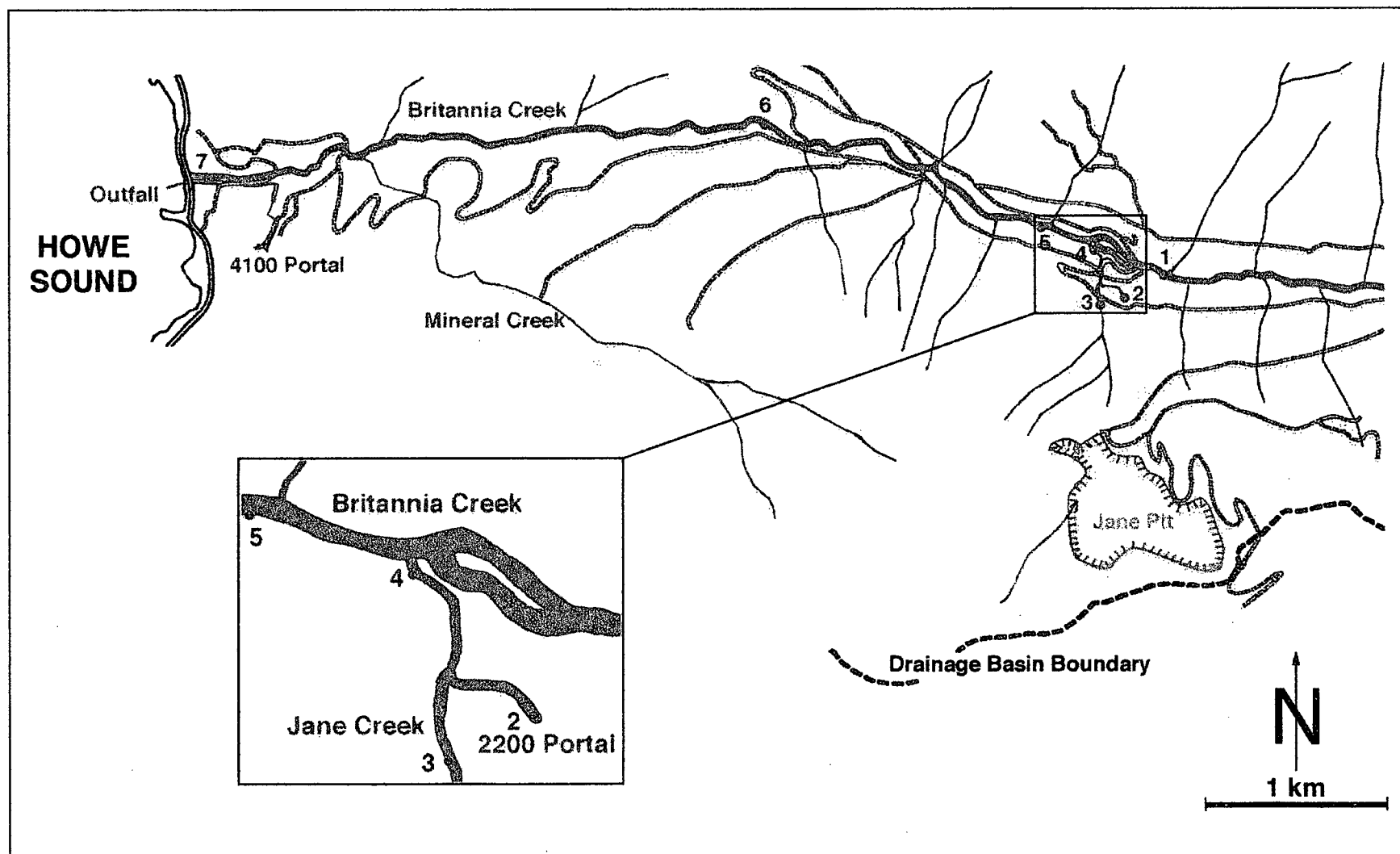
Figure 3.7. Sampling sites at the 2200 portal, in Jane Creek and along Britannia Creek. Water courses are in blue, roads in red. Adapted from Price et al. (1995).

Site	pH	Cu	Cd	Zn	Fe	Al
1	6.98	89	n.m.	87	16	31
2	3.11	100	100	100	97	100
3	7.05	68	99	98	<2	5.2
4	3.60	100	100	100	52	99
5	4.82	97	100	100	11	58
6	5.99	98	100	100	17	20
7	6.40	92	100	99	13	6.5
8	7.09	97	n.m.	97	33	63

Table 3.4. pH and percentage of metal present in dissolved ($< 0.4\ \mu$m) form in samples of acid mine drainage and Britannia Creek. Site 8 is at the mouth of Furry Creek some 5 km south of Britannia Beach. For site locations refer to the map in Figure 3.7. n.m. = not measured.

Figure 3.8 shows both the partitioning of metals between the dissolved and particulate phases, and a mass balance for the AMD input calculated using Cd as a conservative tracer. Precipitation of Fe is apparent upon mixing of AMD with creek water. This is reflected by extensive ochre coatings on rocks and the stream bed at the respective sites. Al is also precipitated, but at a later stage which corresponds to a higher pH. In contrast to Fe and Al, Cu remains mostly in the dissolved phase. However, about 26% of the total Cu load is lost by the time Britannia Creek reaches its mouth, suggesting that despite the relatively small proportion being present as suspended particles there is still some removal, for example via adsorption onto iron oxyhydroxide coatings in the creek bed. Such concretion processes were invoked by Chapman et al. (1985) to explain losses of Cu in a stream receiving AMD. With Fe and Al, the losses relative to the primary AMD input amount to 57% and 26%, respectively. These values account for the presence of considerable amounts of Fe and Al in Britannia and Jane Creeks even without input of
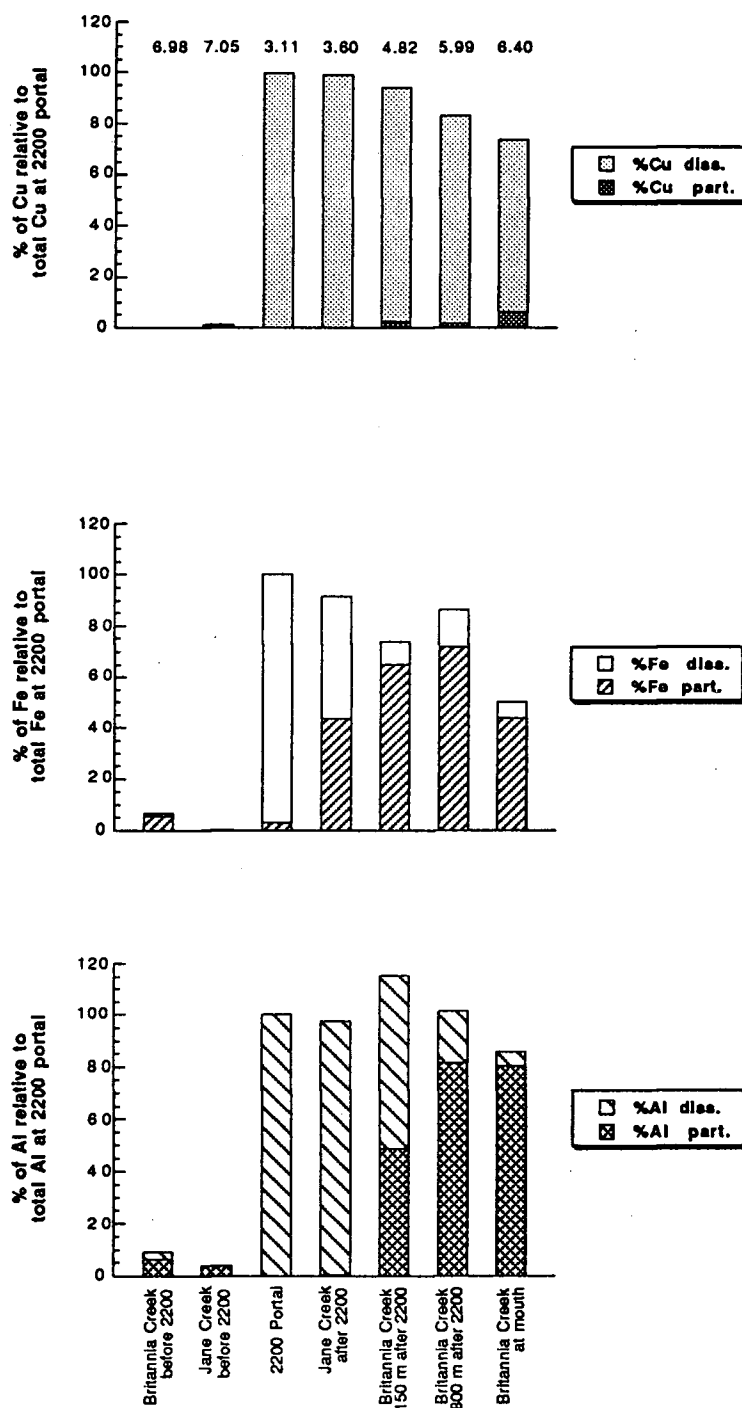
Figure 3.8. Dissolved and particulate metal loads in Britannia and Jane Creeks relative to the input load from the 2200 portal. For the samples after the 2200 portal, numbers below 100% indicate losses of metals, presumably via sedimentation of particles to the creek bed and precipitation onto rock surfaces. Note that creek sources for Cu are insignificant, while they are not negligible for Al, causing total Al to exceed 100% downstream of the 2200 portal.

AMD, but neglect inputs by small tributaries downstream of the confluence with Jane Creek. The observed behaviour of Cu and Fe is in agreement with solubility calculations, which will be discussed in Section 4.3.2. Essentially, they show that Fe is saturated with respect to hydroxides in all samples, while Cu reaches saturation only in the two lower creek stations 6 and 7 in Figure 3.7.

3.3.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on particulate matter collected on filters in order to get more information about the nature and characteristics of the particles in several samples across the mixing zone of Britannia Creek. Some representative examples from the September 1994 transect are shown in Figure 3.9. The corresponding particulate metal and ancillary data are listed in Table 3.5.

Sample location	Estuary	Lower mixing zone	Upper mixing zone	Creek
Sample label	C1	C10	C6	C8
Salinity [‰]	17.00	6.80	1.06	0.07
pH	7.95	8.12	7.41	7.14
chl. a [µg/L]	0.70	0.99	0.15	0.17
DOC [mg C/L]	1.5	7.4	1.7	0.81
Cu part. [µg/L]	0.25	49	72	61
Cd part. [µg/L]	0.0006	0.0017	0.0038	0.0049
Zn part. [µg/L]	0.34	4.9	3.8	2.8
Fe part. [µg/L]	74	82	63	57
Al part. [µg/L]	83	136	188	186

Table 3.5. Particulate metal concentrations and ancillary data for the samples presented in Figure 3.9. The value for DOC in C10 appears anomalously high, however we have no evidence to reject it as contaminated.

Particulate matter in seawater samples was dominated by aluminosilicate grains of 1 - 10 µm in size, although occasionally larger platelets up to 30 µm were also observed. Since the filters were not washed before drying to prevent loss of sample, salt crystals
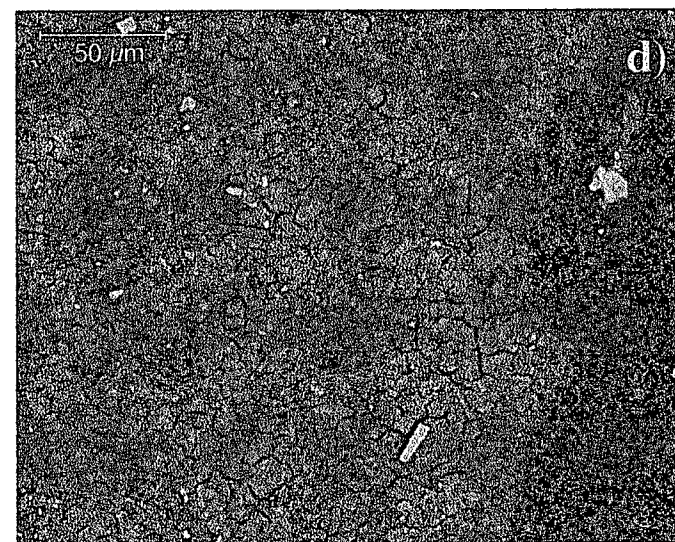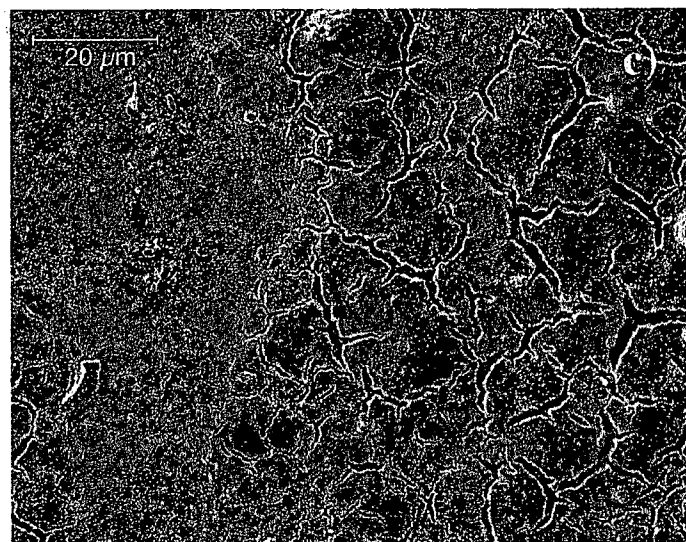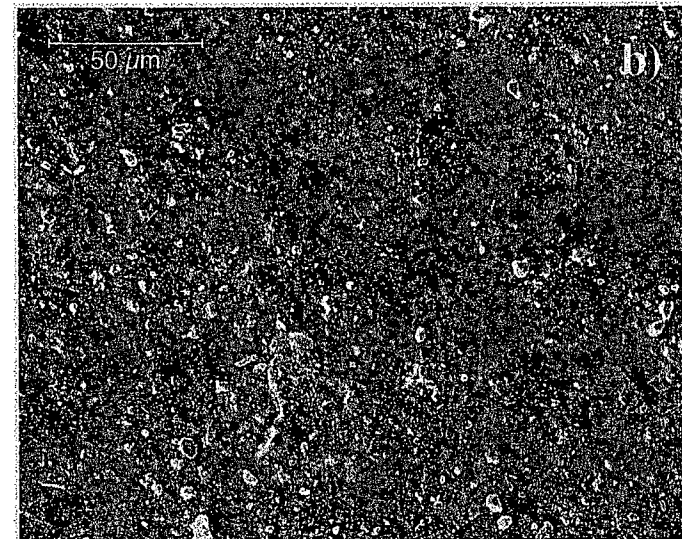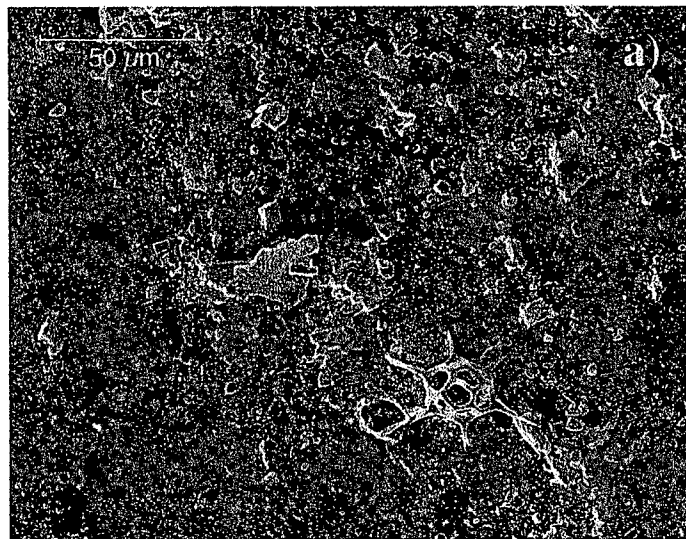
Figure 3.9. Scanning electron micrographs of particulate matter on filters from a surface transect collected in September 1994. Samples represent a) Howe Sound, b) lower mixing zone, c) upper mixing zone, and d) Britannia Creek. Magnification is 500x, except c) 1000x.

accordance with the low chlorophyll a measured in the water samples (Table 3.5). When moving towards the creek, particles became smaller, and biogenic particles disappeared completely. These filters were covered with a thin layer of very fine-grained material. Some larger particles of up to about 4 µm were also present (Figure 3.9). Energy-dispersive X-ray spectra on large filter areas (Figure 3.10) revealed the presence of Al, Si and O in all samples, representing the expected background of aluminosilicates. The samples from the creek and the upper mixing zone had higher Al/Si ratios than their seawater counterparts, which probably reflects the precipitation of Al hydroxides in Britannia Creek. Cu peaks were also higher in these samples, consistent with the results of the chemical analysis. Fe abundance did not change much over the transect, which again is in line with the results displayed in Table 3.5.

The particles in Britannia Creek appear to be distinctly different from those in Britannia Bay surface water. Large catchment basins and the presence of glaciers lead to high suspended matter loads in the Squamish River, which in turn delivers its load of fine grained aluminosilicates to the surface waters of Howe Sound. Britannia Creek in contrast is a clear creek with little suspended terrigenous sediment, and flocculated metals, particularly Al and Fe hydroxides, make up most of its particle pool.
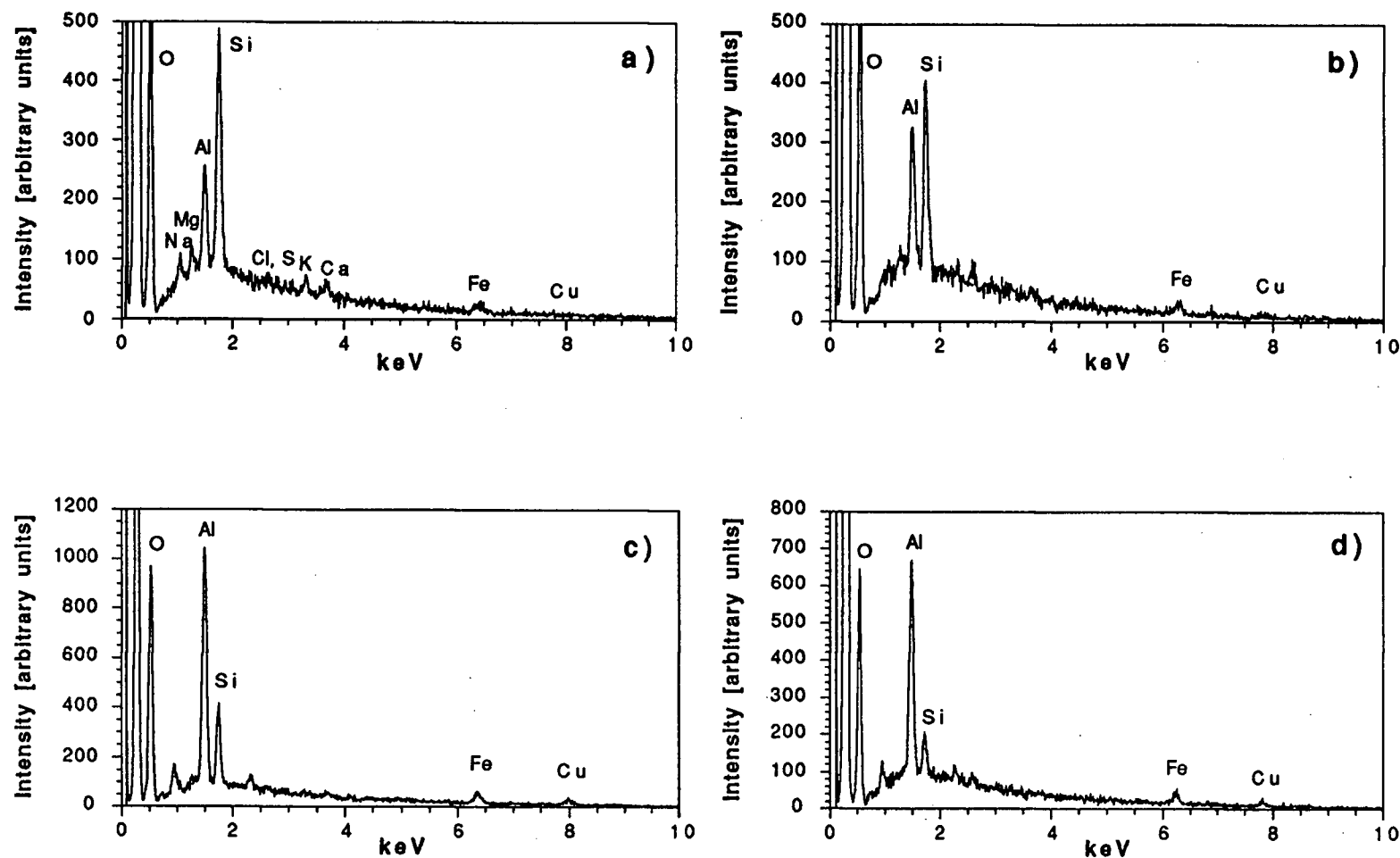
Figure 3.10. Energy-dispersive X-ray spectra of bulk filter surfaces. The samples are identical to those in Figure 3.9, and were taken in a) Britannia Bay, b) lower mixing zone, c) upper mixing zone, and d) Britannia Creek.

3.4. Discussion

Several mechanisms can lead to the removal of metals in the estuarine mixing zone. These include adsorption, precipitation, coagulation, and complexation by adsorbed and flocculating organic ligands. The relative importance of each of these mechanisms with respect to metal removal during the estuarine mixing of Britannia Creek can be inferred from field data and the results of the mixing experiments, as will be discussed in the following sections.

3.4.1. Adsorption

As mentioned earlier, there is ample evidence for adsorption of metals by particles. Of particular interest in a mine setting are iron oxyhydroxides, due to their abundance and their well-known scavenging efficiency. For example, Johnson (1986) found that in a stream contaminated with acid mine drainage, Cu and Zn concentrations were regulated by adsorption onto iron oxyhydroxides. Numerous laboratory investigations have been published on the subject, but for several reasons their results cannot be directly translated to the Howe Sound case. First, most of the experiments were performed at iron concentrations much higher than those encountered in the field (e.g. 0.09 M: Kinniburgh et al. (1976), 2×10^{-3} M: Davis and Leckie (1978), 1×10^{-3} M: Benjamin and Leckie (1981b), 6×10^{-3} M: Balistrieri and Murray (1982)), whereas in this study the concentration range was 0.5 to 18×10^{-6} M. Second, while the literature reports consider cases where the surface sites on iron oxyhydroxides are not saturated and particulate iron concentrations exceed those of the adsorbent, here molar ratios with Cu close to unity are found in many cases. Ratios in the literature are much lower, for instance 1.3×10^{-3} (Kinniburgh et al. 1976), 5×10^{-4} (Davis and Leckie 1978), 5×10^{-2} to 5×10^{-4} (Benjamin and Leckie 1981b), 5×10^{-3} to 5×10^{-5} (Balistrieri and Murray 1982), 0.03

(Millward and Moore 1982), and 5×10^{-3} (Laxen 1985). Since the extent of metal adsorption at a given pH changes among other things with concentration of iron oxyhydroxides and adsorbent/adsorbate ratio, it is difficult to infer metal adsorption in Britannia Creek using literature data.

In the absence of other removal mechanisms, molar ratios close to one as found with Cu (Table 3.6) imply that on average there is one metal atom associated with every atom of particulate iron, including those Fe atoms that are part of the bulk solid below the surface. Even when considering that adsorbing metals may become part of the bulk particle (surface precipitation model, Farley et al. 1985), these ratios seem too high to explain Cu removal by adsorption onto iron oxyhydroxides alone. However, no literature data on maximum adsorptive capacities of iron oxyhydroxides were found to prove or disprove this.

	Cu/Fe	Cd/Fe	Zn/Fe
mean	0.26	1.5×10^{-5}	0.019
range	0.0013 - 1.1	$(1.8 - 6.7) \times 10^{-5}$	0.0007 - 0.099

Table 3.6. Mean and range of molar particulate metal ratios in 13 surface transects across the mixing zone of Britannia Creek.

As has become evident in the SEM study, aluminium-bearing particles, most likely hydroxides, are also present, their concentrations generally exceeding those of Fe by a factor of two. Adsorption edges of Cu and Zn on Al and Fe oxyhydroxides under the same experimental conditions are quite similar (Kinniburgh et al. 1976), as are intrinsic surface complexation constants for amorphous $Fe_2O_3 \cdot H_2O$ and $\gamma\text{-}Al_2O_3$ (Davis and Leckie 1978). Thus, it is conceivable that adsorption onto Al phases could contribute to the removal of Cu, Cd and Zn. However, in mixing experiments the amount of Al flocculated decreased rapidly with salinity above about 3‰, while at the same time the amount of Cu, Cd and Zn flocculated increased (Figure 3.11). This behaviour was

observed with both filtered and unfiltered solutions, indicating that adsorption onto flocculating or pre-formed Al-phases (clays, Al-precipitates from the creek) is not likely to control the removal of Cu, Cd and Zn.

Both End-Members Filtered

Both End-Members Unfiltered
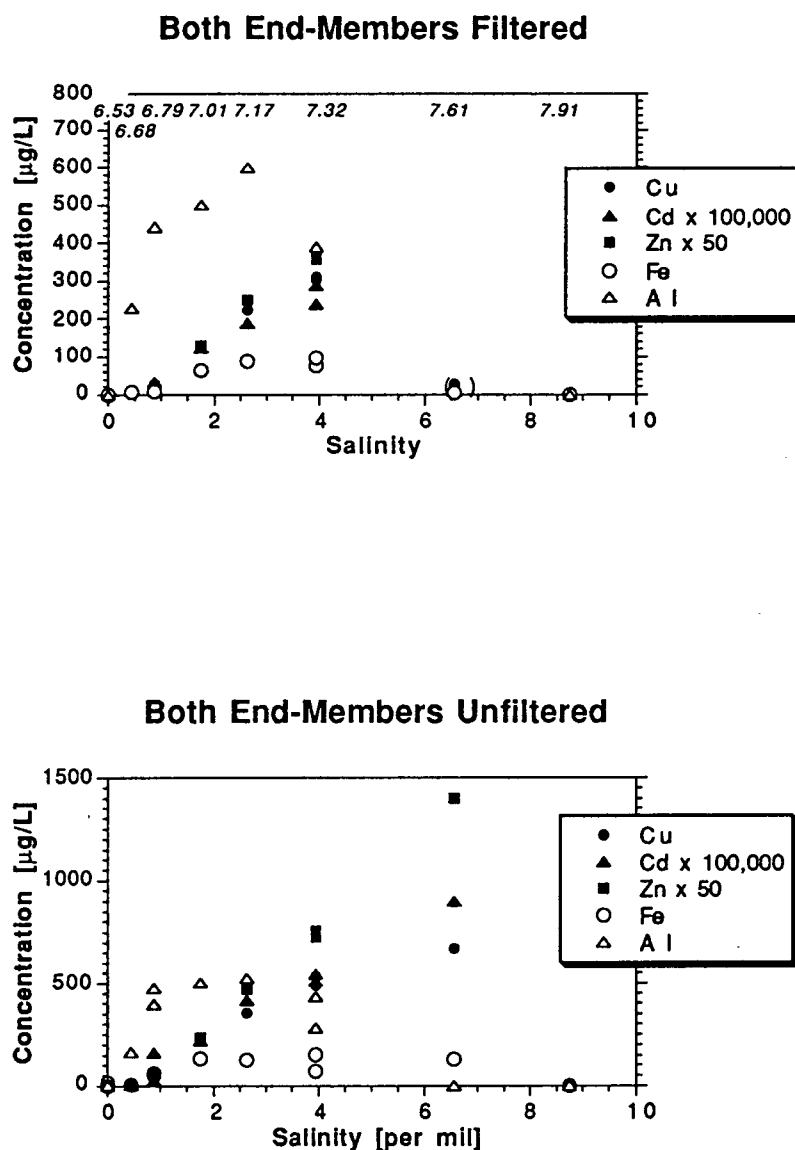
Figure 3.11. Concentration of flocculated Fe, Al, Cu, Cd and Zn (in μg/L creek water) in mixing experiments using filtered (top) and unfiltered (bottom) Britannia Creek water and Howe Sound water. All concentrations are corrected for the amount of particulate metal present in the end-members. The pH of each mixture is shown above the individual symbols in the top panel. The values in brackets are inconsistent with the general trend, however we have no evidence to dismiss them as erroneous.

3.4.2. Precipitation

Since adsorptive reactions alone might not be capable of removing metals to the extent observed, other mechanisms have to be considered. Cu, Cd and Zn all form insoluble complexes with several of the major anions in natural waters, including hydroxide, sulphate, carbonate and chloride. Whether or not these solids actually precipitate under a given set of conditions can be evaluated by calculating the ion activity product (IAP) and comparing it with the standard equilibrium constant K_{s0} for dissolution of the complex (Stumm and Morgan 1996). For the dissolution of a solid under standard conditions according to

$$M(OH)_n(s) \rightarrow M^{n+} + nOH^-, \tag{3.2}$$

the Gibbs free energy is given by

$$\Delta G^\circ = -RT \ln K_{s0}^\circ \tag{3.3}$$

with R = gas constant (8.31 J K^{-1} mol^{-1}), T = temperature in K and

$$K_{s0}^\circ = \frac{\{M^{n+}\}_{eq} \{OH^-\}_{eq}^n}{\{M(OH)_n\}_{eq}} = \{M^{n+}\}_{eq} \{OH^-\}_{eq}^n = IAP_{eq} \tag{3.4}$$

Likewise, an IAP_{act} for the actual measured ion activity can be defined. (In practice, as is done here, the IAP is often calculated from dissolved concentrations, since the activity of the free ions is not easily measured. This issue will be addressed later.) The overall free energy is then given as:

$$\Delta G = \Delta G^{\circ} - \Delta G_{act} = -RT\left[\ln\left(K_{s0}^{\circ}\right) - \ln\left(IAP_{act}\right)\right] = RT\left[\ln\left(IAP_{act}/K_{s0}^{\circ}\right)\right]$$
$$= RT[SI] \tag{3.5}$$

where SI = saturation index. If SI = 0, the reaction is at equilibrium (ΔG = 0). In the case of SI > 0, the actual ion activity product exceeds the solubility at equilibrium, and the solution is supersaturated. Likewise, if SI < 0, dissolution should occur.

Table 3.7 gives the solubility of possible solids with Cu, Cd and Zn under conditions typically encountered in the creek and in Britannia Bay surface waters. It is apparent that precipitation is most likely to occur in the mixing zone or in seawater rather than in Britannia Creek. Several Cu species are supersaturated, while precipitation is not indicated for any of the Cd and Zn species. Whether Cu will precipitate and which complex will form not only depends on thermodynamical, but also on kinetic properties. Therefore, a species that is only slightly supersaturated can precipitate earlier than a kinetically hindered species with a high SI. In the following paragraphs, only the solubility of hydroxides will be considered, since it permits direct comparison between Cu, Cd, Zn and Fe with respect to their tendency to form solid phases. It should be noted, however, that the precipitate that actually forms may well be a Cu carbonate or sulphate rather than a pure hydroxide.

In Figure 3.12, the solubility of the hydroxides of Cu, Cd, Zn and Fe is shown over a range of pH and metal concentrations. There is clear evidence that Cu in field samples is supersaturated with respect to $Cu(OH)_2$ in the mid-range of the samples, corresponding to intermediate salinities (progress of mixing). Cd and Zn in contrast appear to be undersaturated throughout with respect to their solid hydroxide phases. This agrees with the observation that Cu is more extensively removed than Zn, even though their dissolved concentrations are similar. Fe is supersaturated with respect to $Fe(OH)_3$ in all samples. This is a necessary condition for its observed rapid removal in the mixing zone and serves

as additional evidence for the presence of iron oxyhydroxide particles, which may be involved in the adsorptive removal of other metals.

	Creek	Mixing Zone (10‰)	Bay (20‰)	Solid Species	log K_{s0}	SI Creek	SI Mixing Zone	SI Bay
Cu	2×10^{-5}	6×10^{-6}	2×10^{-7}	$Cu(OH)_2$	-19.3	-1.4	0.1	0.2
				$Cu(CO_3)$	-9.6	-9.9	-8.1	-7.5
Cd	3×10^{-8}	2×10^{-8}	1×10^{-9}	$Cu_2(OH)_2CO_3$	-33.8	1.0	2.7	2.7
				$Cu_2(OH)_2(CO_3)_2$	-46.0	1.1	3.9	3.1
Zn	1×10^{-5}	5×10^{-6}	3×10^{-7}	$Cu_4(OH)_6SO_4$	-68.6	-1.6	3.5	2.7
				$Cd(OH)_2$	-14.3	-9.2	-7.4	-4.8
OH⁻	1×10^{-8}	1×10^{-7}	6×10^{-7}	$Cd(CO_3)_2$	-13.7	-8.6	-6.4	-5.7
CO_3^{2-}	4×10^{-8}	6×10^{-7}	6×10^{-6}	$Zn(OH)_2$	-15.5	-5.5	-3.8	-3.5
SO_4^{2-}	4×10^{-4}	6×10^{-3}	2×10^{-2}	$Zn(CO_3)_2$	-10.0	-9.8	-7.7	-6.9
Cl⁻	2×10^{-4}	0.1	0.3	$Zn_2(OH)_3Cl$	-26.8	-10.9	-5.8	-5.4

Table 3.7. Calculation of saturation indices (SI) of likely solid phases in Britannia Creek, its mixing zone, and in Britannia Bay. All concentrations are in mol/L. Metal values are typical total dissolved concentrations in field samples. Anion concentrations were obtained from field data (OH⁻), or estimated from data by Price et al. (1995, SO_4^{2-} in creek) and Livingstone (1963, other creek anions). Anion concentrations in Britannia Bay and in the mixing zone were calculated from the average seawater composition at a salinity of 35‰ (Stumm and Morgan 1996), accounting for dilution with freshwater containing 7×10^{-4} M CO_3^{2-}, 3×10^{-4} M SO_4^{2-} and 2×10^{-4} M Cl⁻ (Livingstone 1963). K°_{s0} data are from Morel and Hering (1993). Saturation indices were calculated according to Equation 3.5 from the respective concentrations.

The solubility lines in Figure 3.12 are calculated for ionic strength = 0. Activity coefficients at 20‰ salinity (I = 0.4) were estimated both by using the data of Whitfield (1975) and the Davies equation. The decrease of the activity coefficients at higher ionic strength leads to a small shift of the solubility lines towards higher pH in the area of interest, corresponding to slightly higher solubility. However, most of the data points for

a)

b)
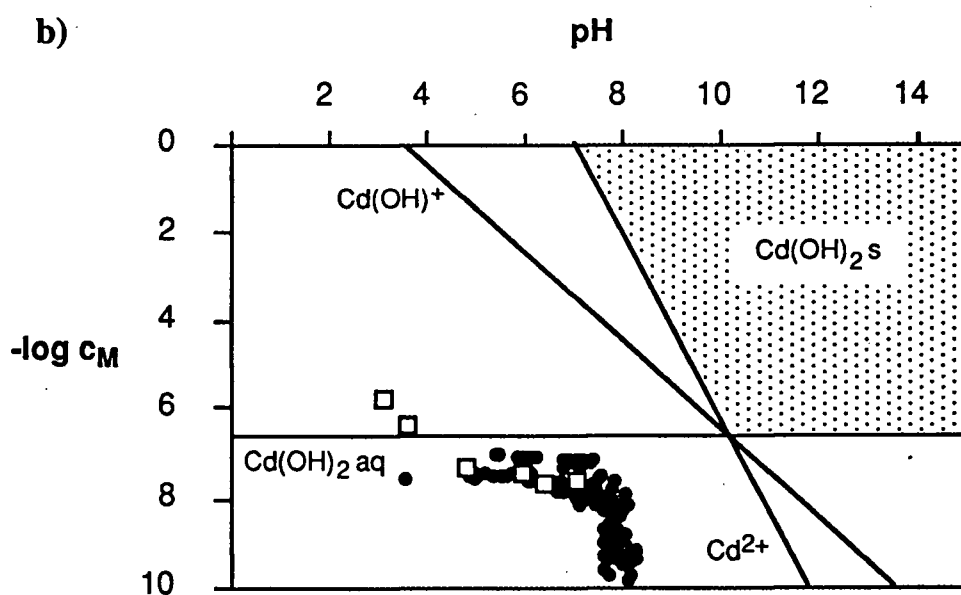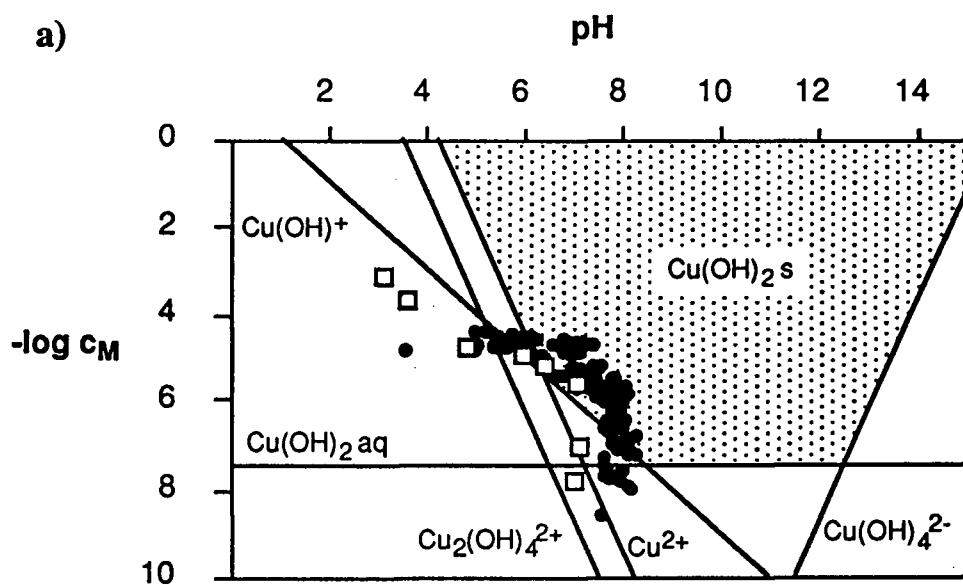
Figure 3.12. (continued next page)
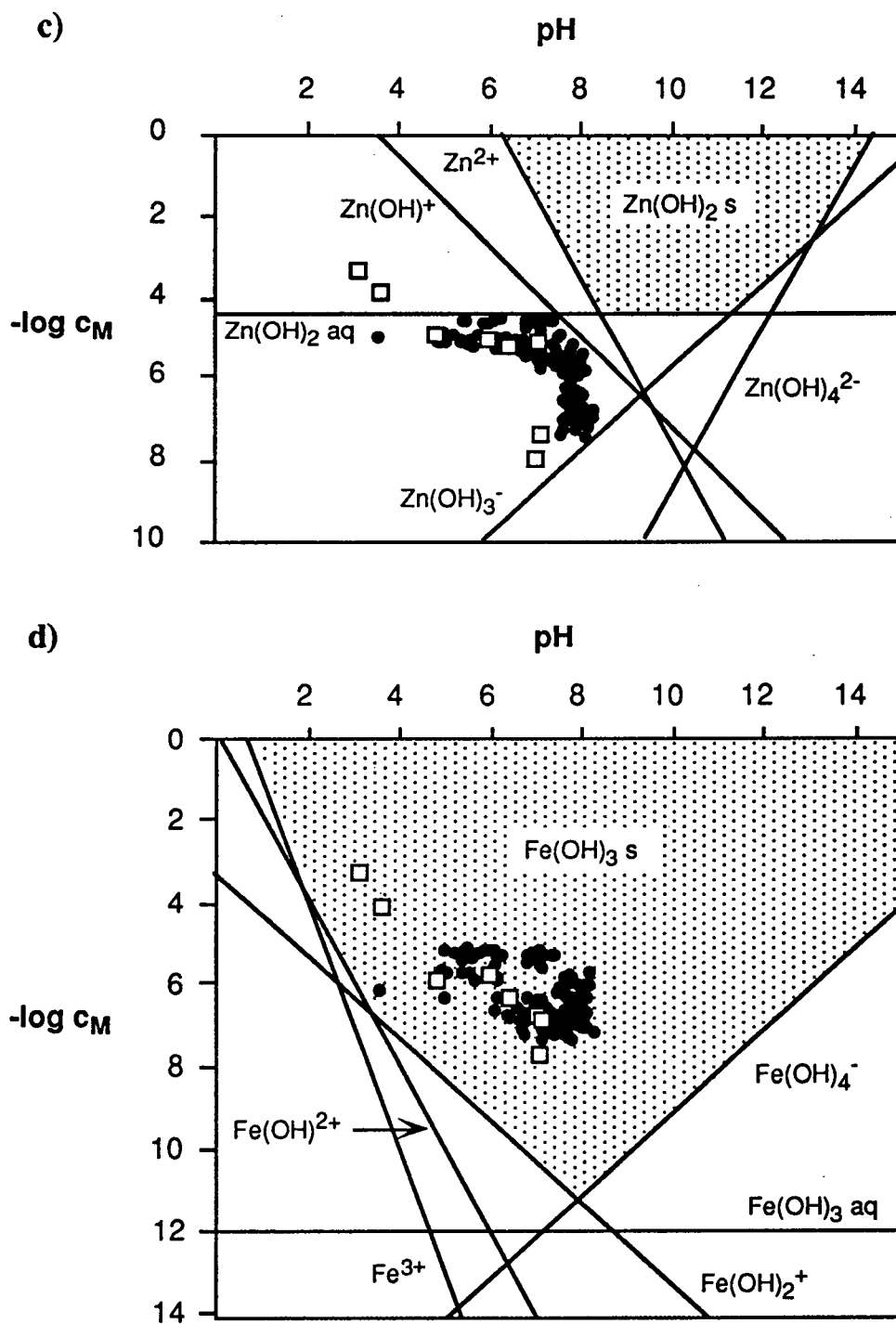
Figure 3.12 (continued). Solubility diagrams for hydroxides of a) Cu, b) Cd, c) Zn and d) Fe in surface transects (solid circles). Open squares denote samples from AMD and Britannia Creek taken in February 1996. The data represent total dissolved metal concentrations. Redrawn after Stumm and Morgan (1996) using constants from Morel and Hering (1993).

Cu still fall well within the zone of supersaturation. For Cd and Zn, the ionic strength correction leads to even more pronounced undersaturation.

The calculations were all based on total dissolved (< 0.4 μm) concentrations, neglecting colloidal contributions to the dissolved phase. In the case of Cd and Zn, taking this into account would again increase undersaturation. With Cu, the computer code MINTEQ.A2 was used with the data from the June mixing experiment to calculate the concentration of dissolved Cu species at the point of equilibrium with respect to precipitation of hydroxides. It was found that at equilibrium, only about 30% of the measured dissolved Cu was present as truly dissolved species, while the remainder precipitated and formed colloids. Although quite low, the dissolved inorganic Cu concentration calculated in this manner agrees well with the labile Cu concentration as measured in the same samples by a diffusive gel technique, as will be shown in Chapter 4. This suggests that Cu may in fact be present to a large degree in colloidal form, consistent with the findings from the January mixing experiments (Section 3.3.1.3. and 3.3.1.4.).

Coprecipitation of metals is known to be important in soil solutions (Bourg 1988) and has been invoked as another possible removal mechanism in estuaries (Laxen 1985). The most likely candidates for coprecipitation are Fe and Cu, since both are supersaturated with respect to their hydroxides. However, the mixing experiments have shown independent behavior of Cu and Fe with respect to flocculation; hence coprecipitation is not likely a major contributor to the overall removal of these two metals .

3.4.3. Particle Effects

The mixing experiments demonstrated that more metal flocculated in the presence of particles compared to when filtered end-members were used (Figure 3.3). This is understandable when considering that adsorptive processes require the presence of reactive surfaces. Surprisingly though, there was virtually no difference in the removal efficiency of creek-derived and estuarine particles. These results are summarized in Table 3.8. The nature of the particles does not seem to influence removal efficiency, rather the issue is whether there are any particles present at all. This agrees with the findings of Aston and Chester (1973), who reported that the rate and extent of iron flocculation was strongly dependent on particle concentration. There are several ways by which nonspecific particles could enhance metal removal:

1. by providing surfaces for the adsorption of FeOOH and organic ligands, which in turn complex metals;

2. by promoting aggregation of metal-bearing colloids by providing reactive surfaces and increasing collision frequency; and/or

3. by acting as nucleation centres for supersaturated metals (for example $Cu(OH)_2$). It is known that precipitation of crystalline phases from saturated solutions is often kinetically hindered in the absence of reactive surfaces (Stumm and Morgan 1996).

Although the mixing experiments do not allow us to distinguish between these mechanisms, they can be used to explain the dependence of metal removal on the presence of particles. The kinetics experiment showed that after initial rapid flocculation, more Cu and Zn flocculated after a period of aging (Figure 3.4). This second stage could be caused both by slow coagulation of colloidal particles or by the hindered kinetics of crystal formation. Since the second stage was less pronounced with Fe than with Cu and since the concentration of flocculated Cu exceeded that of Fe, the observed additional flocculation of Cu does not appear to be the result of adsorption onto iron oxyhydroxides.

Rather, Cu seems to be present as some colloidal phase which slowly forms larger aggregates, or as truly dissolved metal in an supersaturated solution; in other words, mechanisms 2) and 3) may be responsible for enhanced removal of Cu in the presence of particles. In contrast, the additional flocculation of Zn is consistent with adsorption onto iron oxyhydroxides or other particulate phases that formed *in situ.* Since Zn is not saturated with respect to its hydroxides, its additional removal in the presence of particles is likely a result of mechanisms 1) and 2).

Collection date	Experiment	%Cu flocc.	%Cd flocc.	%Zn flocc.
Jan. 1996	both end-members filtered	0.4	b.d.	0.08
June 1996	both end-members filtered	26	0.11	2.8
June 1996	creek water filtered	37	0.16	4.3
June 1996	seawater filtered	36	0.19	4.6
June 1996	both end-members unfiltered	44	0.29	5.8
June 1996	AMD filtered	20	0.05	1.0
June 1996	AMD/sewage filtered	51	≈ 1	3.7

Table 3.8. Maximum amount of metal flocculated in mixing experiments, expressed as percentage of the dissolved metal concentration in the freshwater end-member (Britannia Creek, AMD or AMD/sewage mixture, respectively). Values were calculated according to eqn. 2.5 (Chapter 2). b.d. = below detection (part. Cd < 0.002 μg/L). The percentages given for the AMD/sewage mixture include metal flocculated upon mixing of the two freshwater end-members before addition of saltwater. In this experiment, 1.2% of Cd removal was observed during initial mixing of AMD and sewage. Upon mixing with seawater, some release occurred, leading to an overall removal efficiency of 0.76%.

3.4.4. Complexation by Organic Matter

An estimate of the extent of metal removal by flocculating organic matter can be obtained from total particulate carbon (assumed to equal particulate organic carbon) determinations in mixing experiments. Organic matter in the June experiment behaved non-conservatively (Figure 3.13), and about 0.5 mg C/L was flocculated during mixing. An upper limit on the metal-binding capacity of POM can be obtained by assuming that POM consists of 50% C, that all particulate organic carbon is humic substances, that the ratio between humic and fulvic acids is 1:9, that the average metal:ligand stoichiometry is 1:1 (all assumptions after Tessier et al. 1996), and that the equivalent weights (molar weight per gram humic substance) of humic and fulvic acids are 15,000 and 1500, respectively (Tipping 1994). Hence, the flocculated POC represents about 6×10^{-7} mol binding sites per litre of creek water. For comparison, the concentration of Fe flocculated was about 2×10^{-6} mol/L. The similar concentration of organic binding sites and particu-
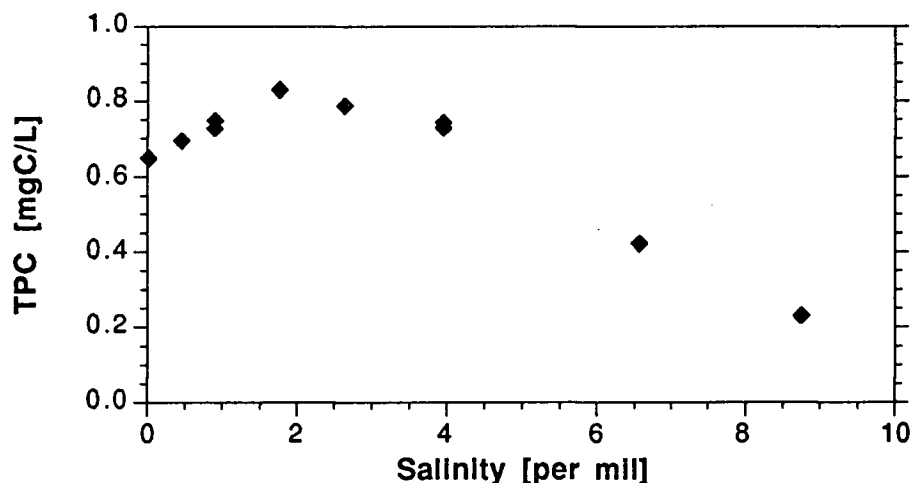
Figure 3.13. Concentration of total particulate carbon (TPC) in mixing experiments performed in June 1996. Unfiltered Britannia Creek and Howe Sound water were used.

late Fe suggests that both adsorption onto iron oxyhydroxides and complexation by flocculating organic matter may contribute to the removal of Cu, Cd and Zn. The lesser tendency of Cd and Zn to bind with organic ligands relative to Cu (Sholkovitz 1978, Buffle 1988) is in agreement with the small degree to which these metals are removed from solution during mixing.

The maximum adsorptive capacity of goethite in freshwater may be around 30 mg humics/g goethite (Tipping 1981), which by using the above assumptions translates to 3×10^{-3} mol organic binding sites per mol Fe. This is two orders of magnitude less than the ratio of 0.3 obtained using the concentrations of POC and particulate Fe in the mixing experiment. It would therefore appear that the removal of dissolved organic matter during mixing must be additionally governed by processes other than adsorption onto iron oxyhydroxides. Preston and Riley (1982) have shown that while Al-hydroxides are not effective scavenging surfaces for organic matter, DOM is removed from solution at high salinity via adsorption onto clays. Given the dependence of silt concentrations in Howe Sound surface waters on Squamish River discharge, the flocculation of DOM and with that its contribution to metal removal may be strongly seasonally controlled.

The mixing experiments do not allow assessment of the relative contributions of organic matter and iron oxyhydroxides to the removal of Cu, Cd and Zn. In addition, the processes at the iron hydroxide surface, and possibly at other surfaces as well, are very complex. Ali and Dzombak (1996) found that the formation of ternary complexes between iron hydroxide, Cu and organic ligands was not only dependent on pH and the concentration of FeOOH, Cu and ligands, but that in the presence of sulphate they were additionally controlled by competition with $FeOOH-SO_4-Cu$ complexes. The inhomogeneity of humic substances and the multitude of interactions (binary and ternary complexes of various kinds) obviate the precise evaluation of metal association with humics, iron hydroxides and other particulate matter at the present time.

3.4.5. Effect of Sewage

Under a permit issued by the provincial ministry of environment, sewage from the Britannia Beach community is discharged into the marine outfall that carries acid mine drainage from the 4100 portal to Howe Sound. The rationale for doing this was that the low pH of the acid mine drainage might help to precipitate organics, while the high DOM load in sewage would promote metal flocculation.

Field studies in the estuary of a river carrying sewage have in fact shown removal of Fe and Cu, but little removal of Zn (Feely et al. 1983, Paulson et al. 1984). Although Cu may be present to a large degree in colloidal association with organic matter from sewage and thus be subject to removal via aggregation, the mixing experiments of Feely et al. (1983) using the same river water suggest that Cu removal in the presence of sewage is less substantial than anticipated. However, the situation at Britannia differs from the scenario described by Feely et al. (1983) in that there is a strong pH gradient in addition to the salinity gradient, and the effects of both parameters need to be investigated.

The mixing experiments show dramatically enhanced removal of Cu, Cd and Zn (Figure 3.6, Table 3.8) in the presence of sewage. Based on the very different pH regimes between the experiment with and without sewage (Figure 3.6), it was argued earlier that the increased removal efficiency might be brought about by the buffering capacity of the sewage rather than by its organic load. This seems to hold true for Cu, which in most instances is undersaturated with respect to $Cu(OH)_2$ in the absence of sewage (Figure 3.14 a). The one mixture that is supersaturated corresponds to the sample at $S = 6.6\%o$ (Fig. 3.6), which exhibits extensive Cu removal. In the presence of sewage, Cu is supersaturated throughout, consistent with the extensive removal observed. In contrast, Cd and Zn remain undersaturated with respect to their hydroxides despite their high concentrations in AMD, even in the presence of sewage (Figure 3.14 b, c). Fe is supersaturated in all samples (Figure 3.14 d). The high buffering capacity of sewage

results in extensive precipitation of Fe at low salinity as confirmed by particulate Fe determinations and may indirectly control the removal of Cd and Zn via adsorption onto iron oxyhydroxides.

Apart from increasing the pH, the dissolved organic matter in sewage could also affect metal removal by complexation, adsorption and flocculation. In this experiment, 2.8 mg TPC flocculated per litre AMD/sewage mixture, a relatively small increase compared to the 0.5 mg in creek mixing experiments. The difficulties experienced upon filtration of the raw sewage sample lead us to believe that most of the organic matter is present as finely dispersed particles of close to 0.4 μm diameter, and that much more flocculation would be observed were these particles to be left in the sample before mixing. If it is assumed that the organic ligands in sewage are similar to humic substances, the TPC flocculated translates to 3.4×10^{-6} mol ligands/L (see Section 3.4.4), which compares to a flocculated Fe concentration of 4.0×10^{-6} mol/L. The similar concentration of organic binding sites and particulate Fe suggests that organic matter plays a more important role in the removal of metals than in Britannia Creek, where particulate Fe exceeded organic ligand concentrations. The corresponding concentrations of flocculated Cu, Cd and Zn are 4.2×10^{-5}, 2.8×10^{-9} and 5.9×10^{-6} mol per litre AMD/sewage mixture, respectively. The concentrations of iron oxyhydroxides and organic ligands are too small to entirely account for the removal of Cu, and precipitation of solid phases is likely a controlling mechanism for this metal. With Cd and Zn, for which precipitation is not thought to be important, organic ligands are likely to contribute substantially to their removal. The high concentration of organic ligands and the absence of large amounts of silt in sewage suggest that organic matter is not only removed from solution via adsorption onto iron oxyhydroxides, but also via aggregation of colloidal organic particles.

a)

b)
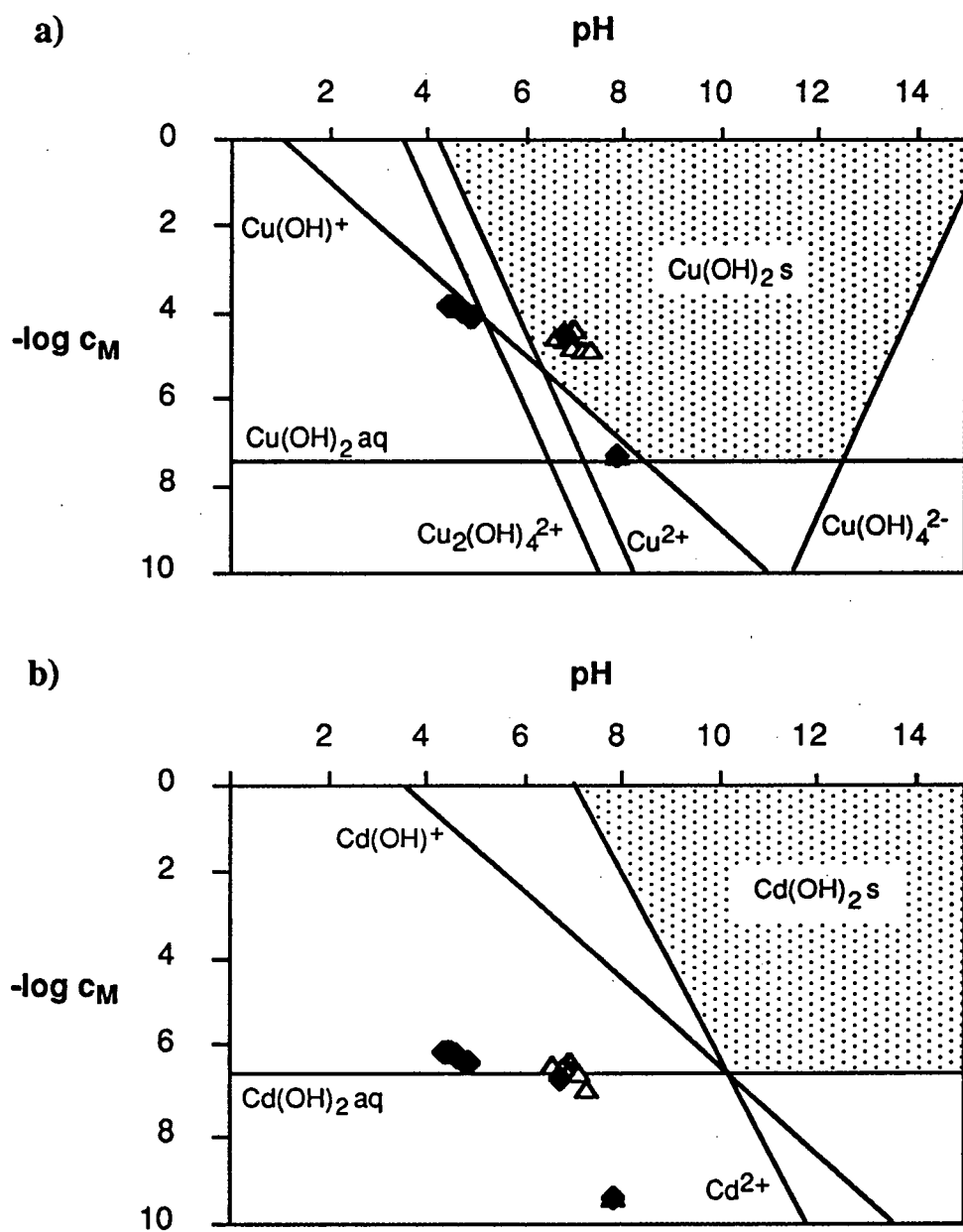
Figure 3.14. (continued next page)

c)

d)
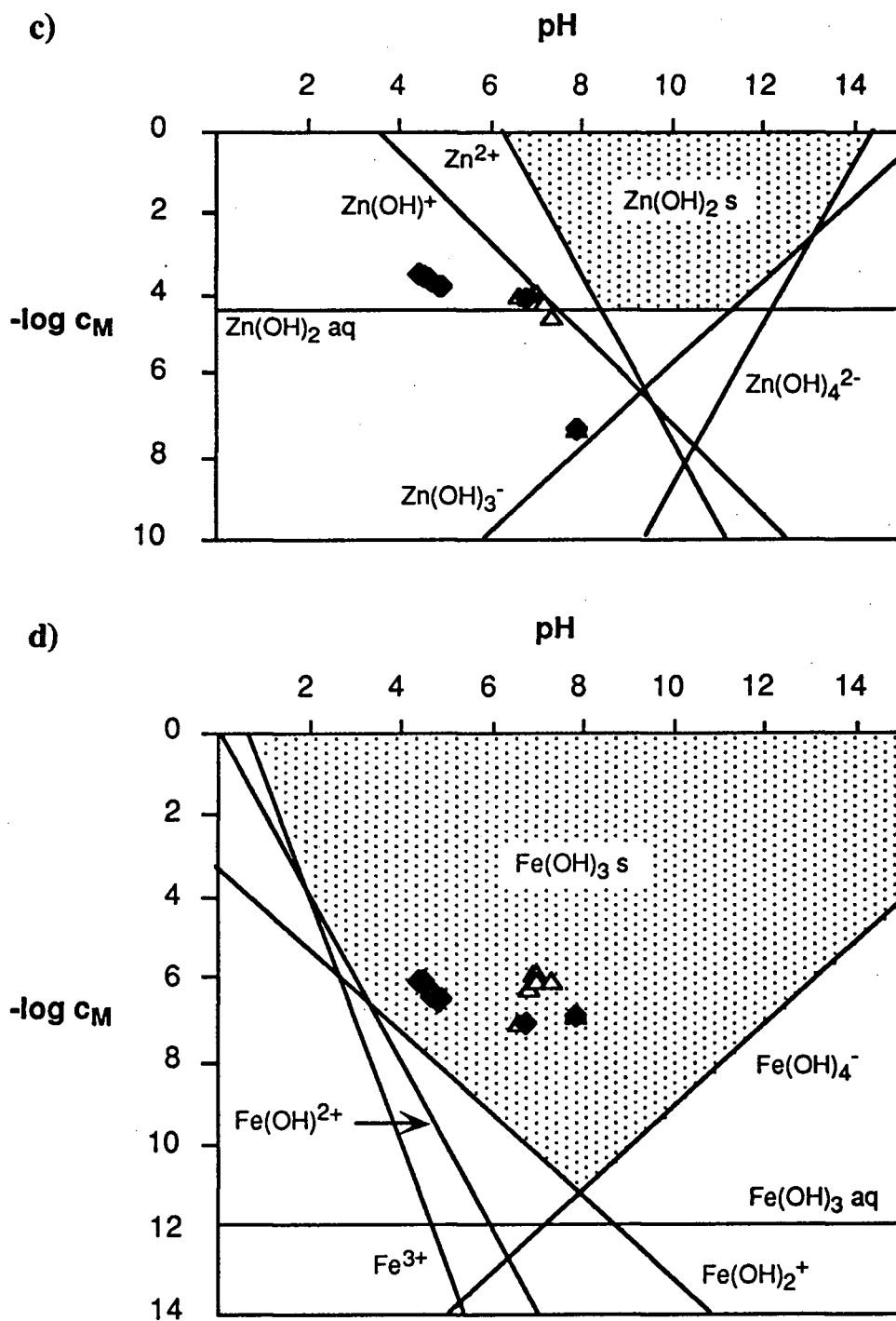
Figure 3.14 (continued). Solubility diagrams for hydroxides of a) Cu, b) Cd, c) Zn and d) Fe in AMD/seawater mixtures (solid diamonds), and in mixtures of AMD/sewage with seawater (open triangles). The data represent total dissolved metal concentrations. Redrawn after Stumm and Morgan (1996) using constants from Morel and Hering (1993).

3.5. Conclusions

The results presented have shown that the removal of Cu in the mixing zone of Britannia Creek may be controlled to a large extent by the precipitation of hydroxides, hydroxy-carbonates and hydroxy-sulphates, while Cd and Zn, which show less removal, are governed by adsorptive processes and complexation by organics. The lesser removal of Cd compared to Zn agrees with its lower tendency to adsorb onto Fe hydroxides (Benjamin and Leckie 1981a, Balistrieri and Murray 1982, Buffle 1988) and clays (Bourg 1988), which may be a result of competition with Mg for surface binding sites (Balistrieri and Murray 1982). While the amount of Cu, Cd and Zn removed during mixing varied seasonally (Chapter 2), the efficiency of the process appears to be constant, as is evident from a linear correlation between the maximum amount flocculated in any month and the dissolved metal concentration in the creek (Figure 3.15). The relationship is tighter for Cu than for Zn and Cd, which is understandable given the small proportions of the latter two metals that actually flocculate. Still, the correlation is remarkable given the seasonal fluctuation of critical parameters such as pH, salinity, suspended solids content and nature of the solids. Ultimately, the covariation between these parameters may be a result of their dependence on the acid mine drainage input. For example, during periods of high Cu concentrations in the creek, pH tends to be lower and particulate Fe and Al higher. Both effects result in increased removal of Cu, Cd and Zn and compensate to some extent for the increased metal load. It must be noted that only the removal efficiency is constant, not the amount delivered to the estuary, so that the load discharged to Howe Sound still depends on the amount of acid mine drainage generated, as discussed in the previous chapter.

In contrast to the findings of Johnson and Thornton (1987) and Karlsson et al. (1987) in streams receiving acid mine drainage, the removal of Cu both in Britannia Creek and in its mixing zone is not primarily controlled by adsorption onto iron oxyhydroxides. This

a)

Cu(flocc.) = -46 + 0.37 x Cu(creek)   R^2 = 0.93

b)

Cd(flocc.) = 0.0016 + 0 0012 x Cd(creek)   R^2 = 0.44

c)

Zn(flocc.) = 1.7 + 0.03 x Zn(creek)   R^2 = 0.87
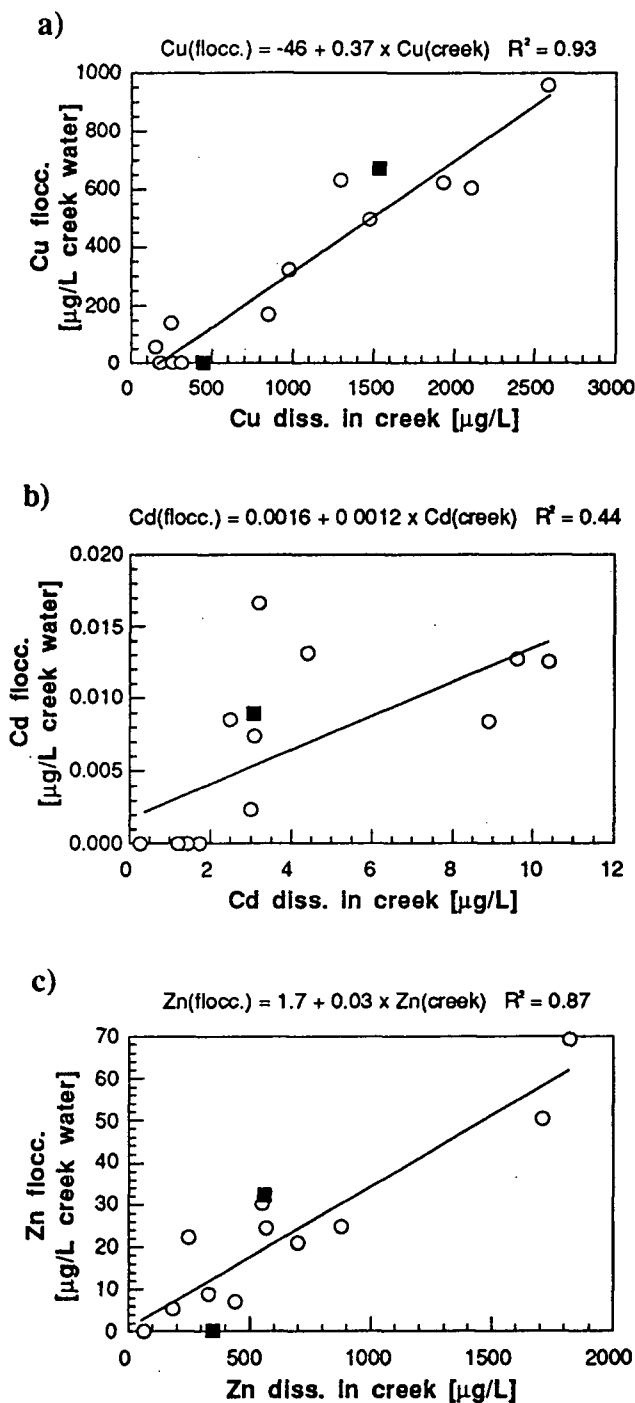
Figure 3.15. Removal efficiency calculated from field transects *versus* dissolved metal concentrations in Britannia Creek. Efficiency is expressed as the maximum amount of metal flocculated upon mixing of 1 L Britannia Creek water with seawater, and was calculated according to equation 2.5 (Chapter 2). The linear regression does not include the samples from the mixing experiments (solid squares). Note that the lower value of them represents the January 1996 experiment with filtered end-members, while in the June 1996 experiment (higher value) unfiltered end-members were used. April 1994 data were excluded.

seems to arise from the low iron content of AMD relative to Cu, so that even when accounting for adsorption by iron oxyhydroxides, dissolved Cu concentrations remain high. In fact, they appear high enough to cause the precipitation of Cu-hydroxides even within the freshwater system. Johnson and Thornton (1987) found that at their study site, a stream receiving AMD, Cu was undersaturated with respect to hydroxides at all times. The situation encountered at Britannia may not represent a typical mine setting, since one would expect an excess of Fe over Cu, but it does show that under certain circumstances chemical precipitation can be just as important for metal removal as adsorptive processes or complexation by organic matter.

The mixing experiments have demonstrated that filterable Fe and Cu are present to a large degree as colloids rather than in true solution, as suggested by earlier work (Sholkovitz and Copland 1981, Hunter 1983, Honeyman and Santschi 1989) and confirmed in recent field studies (Martin et al . 1995, Dai and Martin 1995, Hill and Aplin 1996, Muller 1996, Sañudo-Wilhelmy et al. 1996). This has implications for sampling as well as interpretation of data. Clearly, the operational cutoff between dissolved and particulate phases at a particle diameter of 0.4 µm has no mechanistic justification. However, due to the lack of rapid size-discrimination procedures suited for field use, this cutoff will continue to be applied widely. In order to minimize artefacts arising from the slow aggregation of colloidal material, it is advisable to filter and preserve samples as quickly as possible. Colloidal contributions to the measured "dissolved" phase must also be borne in mind when interpreting data, in order to prevent drawing erroneous conclusions. For example, the calculation of oceanic metal residence times is often based on dissolved concentrations in rivers, and thus may not take into account the flocculation of colloidal metals in estuaries (Sañudo-Wilhelmy et al. 1996).

Metal removal in mixtures of acid mine drainage and seawater gave no indication that different processes might be at work than those observed in the mixing of Britannia Creek water. However, addition of sewage resulted in enhanced metal flocculation due to the

buffering capacity of the sewage and the presence of organic substances. These may not only act as complexing agents, but they could also modify the adsorptive and coagulative properties of particles. Given the enhanced removal observed in the presence of particles in Britannia Creek mixing experiments, removal efficiency might even be higher if unfiltered samples had been used. The results suggest that adding sewage to AMD before discharge to the estuary may be a simple and effective way of reducing the dissolved metal load to Howe Sound. The mixing ratio of 1:1 sewage/AMD used in this experiment is high relative to what can be expected in the field and was chosen such that an effect of the sewage could be clearly demonstrated. Additionally, at Britannia sewage is pumped into the AMD outfall for only a few minutes at a time, at irregular intervals spaced about 15 minutes to several hours depending on water consumption. The effect of sewage on metal removal thus may be not nearly as large as suggested by the experiments. Instead, the benefit of discharging sewage together with AMD may lie in increased complexation of Cu and other metals, which may reduce their bioavailability and hence their potential toxic effects on aquatic organisms.

This chapter has focused on the changes in metal partitioning between dissolved and particulate phases in the mixing zone of Britannia Creek. The gradients in pH, salinity and major ion concentrations between fresh- and saltwater additionally influence the speciation of dissolved metals. Both processes have important toxicological and ecological implications. Changes in metal partitioning determine the amount of metal that remains in the dissolved phase as well as the amount that is ultimately transferred to the sediment. While high dissolved metal concentrations in surface waters may affect fish and planktonic organisms, elevated amounts of suspended particulate metals may be harmful to filter feeders, and high sedimentary concentrations can have adverse effects on benthos. Changes in dissolved metal speciation may alter the toxicity of metals to marine organisms, in particular phytoplankton, for which it has been shown that it is the activity of the free ion, rather than the total concentration, which determines metal toxicity (for a critical

appraisal of the issue see Campbell 1995). The next chapter will address some of these issues and link observed effects of elevated metal concentrations to speciation measurements and calculations.

3.6. References

Adediran, S.A. and J.R. Kramer, 1987. Copper adsorption on clay, iron-manganese oxide and organic fractions along a salinity gradient. Appl. Geochem. **2**, 213 - 216.

Ali, M.A. and D.A. Dzombak, 1996. Interactions of copper, organic acids, and sulfate in goethite suspensions. Geochim. Cosmochim. Acta **60**, 5045 - 5053.

Aston, S.R. and R. Chester, 1973. The influence of suspended particles on the precipitation of iron in natural waters. Estuar. Coastal Mar. Sci. **1**, 225 - 231.

Balistrieri, L.S. and J.W. Murray, 1982. The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater. Geochim. Cosmochim. Acta **46**, 1253 - 1265.

Balistrieri, L.S. and J.W. Murray, 1984. Marine scavenging: Trace metal adsorption by interfacial sediment from MANOP site H. Geochim. Cosmochim. Acta **48**, 921 - 929.

Benjamin, M.M. and J.O. Leckie, 1981a. Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J. Coll. Interf. Sci. **79**, 209 - 221.

Benjamin, M.M. and J.O. Leckie, 1981b. Competitive adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J. Coll. Interf. Sci. **83**, 410 - 418.

Benjamin, M.M. and J.O. Leckie, 1982. Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behavior of Cd on oxide surfaces. Environ. Sci. Technol. **16**, 162 -170.

Bewers, J.M. and P.A. Yeats, 1978. Trace metals in the waters of a partially mixed estuary. Estuar. Coastal Mar. Sci. **7**, 147 - 162.

Bewers, J.M. and P.A. Yeats, 1981. Behaviour of trace metals during estuarine mixing. Proceedings, River Inputs to Ocean Systems, Rome, 103-115.

Bigham, J.M., U. Schwertmann, S.J. Traina, R.L. Winland and M. Wolf, 1996. Schwertmannite and the chemical modelling of iron in acid sulfate waters. Geochim. Cosmochim. Acta **60**, 2111 - 2121.

Bilinski, H., S. Kozar, M. Plavsic, Z. Kwokal and M. Branica, 1991. Trace metal adsorption on inorganic solid phases under estuarine conditions. Mar. Chem. **32**, 225 - 233.

Bladh, K.W., 1982. The formation of goethite, jarosite, and alunite during the weathering of sulfide-bearing felsic rocks. Econ. Geol. **77**, 176 - 184.

Bourg, A.C.M., 1988. Metals in aquatic and terrestrial systems: Sorption, speciation, and mobilization. In: Chemistry and biology of solid waste, W. Salomons and U. Förstner eds., Springer, Berlin, 3 - 32.

Boyle, E.A., S.S. Huested and B. Grant, 1982. The chemical mass balance of the Amazon plume; II, copper, nickel and cadmium. Deep Sea Res. **29**, 1355 - 1364.

Buffle, J., 1988. Complexation reactions in aquatic systems: An analytical approach. Ellis Horwood, Chichester.

Campbell, P.G.C., 1995. Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. In: Metal Speciation and Bioavailability in Aquatic Systems, A. Tessier and D.R. Turner eds., Wiley, New York.

Chapman, B.M., D.R. Jones and R.F. Jung, 1983. Processes controlling metal ion attenuation in acid mine drainage streams. Geochim. Cosmochim. Acta **47**, 1957 - 1973.

Dai, M., J.-M. Martin and G. Cauvet, 1995. The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France). Mar. Chem. **51**, 159 - 175.

Davis, J.A. and J.O. Leckie, 1978. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. J. Coll. Interf. Sci. **67**, 90 - 106.

Duinker, J.C., 1980. Suspended matter in estuaries: Adsorption and desorption processes. In: Chemistry and biochemistry of estuaries, E. Olausson and I. Cato eds., Wiley-Interscience, New York, 121 - 151.

Duinker, J.C., 1983. Effects of particle size and density on the transport of metals to the ocean. In: Trace metals in seawater, C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg eds., Plenum Press, New York, 209 - 226.

Eckert, J.M. and E.R. Sholkovitz, 1976. The flocculation of iron, aluminium and humates from river water by electrolytes. Geochim. Cosmochim. Acta **40**, 847 - 848.

Edmond, J.M., A. Spivack, B.C. Grant, M.H. Hu, Z.X. Chen, S. Chen and X.S. Zhong, 1985. Chemical dynamics of the Changjiang estuary. Sediment dynamics of the Changjiang estuary and the adjacent east China Sea. Cont. Shelf Res. **4**, 17 - 34.

Elbaz-Poulichet, F., J.-M. Garnier, D.M. Guan, J.-M. Martin and A.J. Thomas, 1996. The conservative behaviour of trace metals (Cd, Cu, Ni and Pb) and As in the surface plume of stratified estuaries: Example of the Rhone river (France). Estuar. Coastal Shelf Sci. **42**, 289 - 310.

Eliott, H.A. and C.P. Huang, 1981. Adsorption characteristics of some Cu(II) complexes on aluminosilicates. Water Res. **15**, 849 - 855.

Farley, K.J., D.A. Dzombak and F.M.M. Morel, 1985. A surface precipitation model for the sorption of cations on metal oxides. J. Coll. Interf. Sci. **106**, 226 - 242.

Feely, R.A., G.J. Massoth and M.F. Lamb, 1983. The effect of sewage effluents on the flocculation of major elements in a stratified estuary. In: Trace metals in seawater, C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg eds., Plenum Press, New York, 227 - 244.

Flegal, A.R., G.J. Smith, G.A. Gill and S. Sañudo-Wilhelmy, 1991. Dissolved trace element cycles in the San Francisco Bay estuary. Mar. Chem. **36**, 329 - 363.

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.

Foster, P., T.E. Hunt and A.W. Morris, 1978. Metals in an acid mine stream and estuary. Sci. Tot. Environ. **9**, 75 - 86.

Fox, L.E. and S.C. Wofsy, 1983. Kinetics of removal of iron colloids from estuaries. Geochim. Cosmochim. Acta **47**, 211 - 216.

Hill, D.M. and A.C. Aplin, 1996. Role of colloids as carriers of metals in river waters. S.H. Bottrell ed., Fourth International Symposium on the Geochemistry of the Earth's Surface, Ilkley, U.K., 534 - 536.

Honeyman, B.D. and P.H. Santschi, 1989. A Brownian-pumping model for oceanic trace metal scavenging: Evidence from Th isotopes. J. Mar. Res. **47**, 951 - 992.

Hong, H. and D.R. Kester, 1985. Chemical forms of iron in the Connecticut River estuary. Estuar. Coastal Shelf Sci. **21**, 449 - 459.

Hunter, K.A., 1983. On the estuarine mixing of dissolved substances in relation to colloid stability and surface properties. Geochim. Cosmochim. Acta **47**, 467 - 473.

Hunter, K.A. and P.S. Liss, 1982. Organic matter and the surface charge of suspended particles in estuarine waters. Limnol. Oceanogr. **27**, 322 - 335.

Johnson, C.A., 1986. The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. Geochim. Cosmochim. Acta **50**, 2433 - 2438.

Johnson, C.A. and I. Thornton, 1987. Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. Water Res. **21**, 359 - 365.

Kinniburgh, D.G., M.L. Jackson and J.K. Syers, 1976. Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminum. Soil Sci. Soc. Am. J. **40**, 796 - 799.

Krone, R.B., 1978. Aggregation of suspended particles in estuaries. In: Estuarine Transport Processes, B. Kierfve ed., University of Southern California Press, Davis CA, 177 - 190.

Laxen, D.P.H., 1985. Trace metal adsorption/coprecipitation on hydrous ferric oxide under realistic conditions. The role of humic substances. Water Res. **19**, 1229 - 1236.

Li, Y.-H., L. Burkhardt and H. Teraoka, 1984. Desorption and coagulation of trace elements during estuarine mixing. Geochim. Cosmochim. Acta **48**, 1879 - 1884.

Libes, S.M., 1992. An introduction to marine biogeochemistry. Wiley, New York, pp. 36 and 341.

Livingstone, D.A., 1963. Chemical composition of rivers and lakes. In: Data of Geochemistry, 6th. ed., U.S. Geological Survey Professional Paper, 440-G.

Manahan, S.E., 1991. Environmental Chemistry. 5th ed., Lewis Publishers, Chelsea MI.

Martin, J.-M., M.-H. Dai and G. Cauvet, 1995. Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). Limnol. Oceanogr. **40**, 119 - 131.

Millward, G.E. and R.M. Moore, 1982. The adsorption of Cu, Mn and Zn by iron oxyhydroxide in model estuarine solutions. Water Res. **16**, 981 - 985.

Morel, F.M.M. and J.G. Hering, 1993. Principles and Applications of Aquatic Chemistry. Wiley, New York.

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**, 680 - 682.

Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. Mar. Chem. **52**, 245 - 268.

Paulson, A.J., R.A. Feely, H.C. Curl and J.F. Gendron, 1984. Behaviour of Fe, Mn, Cu and Cd in the Duwamish River estuary downstream of a sewage treatment plant. Water Res. **18**, 633 -641.

Pavlova, V. and L. Sigg, 1988. Adsorption of trace metals on aluminium oxide: a simulation of processes in freshwater systems by close approximation to natural conditions. Water Res. **22**, 1571 - 1575.

Preston, M.R. and J.P. Riley, 1982. The interactions of humic compounds with electrolytes and three clay minerals under simulated estuarine conditions. Estuar. Coastal Shelf Sci. **14**, 567 - 576.

Price, W.A., T. Schwab and N. Hutt, 1995. A reconnaissance study of acid mine drainage at the Britannia mine. B.C. Ministry of Energy, Mines and Petroleum Resources, Victoria, B.C.

Salomons, W. and H. Förstner, 1984. Metals in the hydrocycle. Springer, Berlin,

Sañudo-Wilhelmy, S.A., I. Rivera-Duarte and A.R. Flegal, 1996. Distribution of colloidal trace metals in the San Francisco Bay estuary. Geochim. Cosmochim. Acta **60**, 4933 - 4944.

Sharp, J.H., C.H. Culberson and T.M. Church, 1982. The chemistry of the Delaware estuary: general considerations. Limnol. Oceanogr. **27**, 1015 - 1028.

Shiller, A.M. and E.A. Boyle, 1991. Trace elements in the Mississippi river delta outflow region: behaviour at low discharge. Geochim. Cosmochim. Acta **55**, 3241 - 3251.

Sholkovitz, E.R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim. Cosmochim. Acta **40**, 831 - 845.

Sholkovitz, E.R., 1978. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. Earth Planet. Sci. Lett. **41**, 77 - 86.

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

Sholkovitz, E.R. and D. Copland, 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. Geochim. Cosmochim. Acta **45**, 181 - 189.

Stumm, W.S. and J.J. Morgan, 1996. Aquatic Chemistry. 3rd ed., Wiley, New York.

Swallow, K.C., D.N. Hume and F.M.M. Morel, 1980. Sorption of copper and lead by hydrous ferric oxide. Environ. Sci. Technol. **14**, 1326 - 1331.

Tessier, A., D. Fortin, N. Belzile, R.R. DeVitre and G.G. Leppard, 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements. Geochim. Cosmochim. Acta **60**, 387 - 404.

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

Tipping, E., 1981. The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta **45**, 191 - 199.

Tipping, E., 1994. WHAM - a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Comp. Geosci. **20**, 973 - 1023.

Verardo, D.J., P.N. Froelich and A. McIntyre, 1990. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 analyzer. Deep-Sea Res. **37**, 157 - 165.

Whitfield, M., 1975. The extension of chemical models for seawater to include trace components at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta **39**, 1545 - 1557.

Windom, H., J. Byrd, J. R Smith, M. Hungspreugs, S. Dharmvanij, W. Thumtrakul and P. Yeats, 1991. Trace metal-nutrient relationships in estuaries. Mar. Chem. **32**, 177 - 194.

CHAPTER 4

RESPONSE OF A
NATURAL ASSEMBLAGE OF PHYTOLANKTON
TO ELEVATED METAL CONCENTRATIONS
FROM ACID MINE DRAINAGE

4.1. Introduction

In previous chapters it has been shown that the effluent from Britannia Mine can disperse in Howe Sound surface waters over large distances. Removal mechanisms in the mixing zone reduce some of the dissolved Cu load, but do not greatly affect Zn and Cd. A number of investigations on potentially harmful effects of mine effluents on marine organisms have been carried out, but unfortunately only a fraction of them are available in the open literature. Field studies in Howe Sound (summarized in Table 4.1) demonstrate that filter feeders, benthic organisms and seaweeds have been affected by mine effluent in surface waters or by submerged tailings. Although the effects are most pronounced in the immediate vicinity of the mine, they also propagate down the estuary as shown by elevated metal concentrations in mussels. Bioassay results (Table 4.2) show that Cu levels in the hundreds of μg/L range can be acutely toxic to a wide variety of organisms under the test conditions used. In the present study, mean dissolved Cu concentrations at Station B in Britannia Bay were 23 μg/L, with maxima as high as 232 μg/L, suggesting that detrimental effects to juvenile salmonids and mussels are possible.

At least three reasons justify an investigation of the potential effects of AMD on phytoplankton in the Britannia Bay area. First, high metal concentrations in surface waters are likely to occur in spring and early summer and may interfere with spring phytoplankton blooms. The timing and magnitude of the blooms determines to a large extent the food supply for heterotrophic organisms such as zooplankton, crustaceans and fish. Second, the effects of metals on phytoplankton may be masked by low light levels caused by the high suspended silt load in Howe Sound surface waters. While it is not possible to isolate these effects from the available field observations by Stockner et al. (1977), the issue can be addressed by performing laboratory experiments. Third, phytoplankton may be able to adapt to higher metal levels, as observed in CEPEX

Field Observations

Organism	Observed effect	Comments	Year of study	Ref.
Edible mussel mussel (*Mytilus edulis*)	whole body tissue: Cu content $\geq$ 8 x higher than in lower Howe Sound	no similar effects observed with Zn	1975	1
	gills: Cu content $\geq$ 32 x higher than in lower Howe Sound. Viscera: $\geq$ 50 x	Zn slightly elevated	1977	2
Oyster (*Crassostrea gigas*)	whole body tissue: Cu content $\geq$ 1.8 x higher than in lower Howe Sound	no similar effects observed with Zn	1975	1
Dungeness crab (*Cancer magister*)	whole body tissue: no elevated Cu or Zn content observed		1977	3
Fish and shrimp	very rare both in otter trawls and in submersible observations	likely induced by low bottom water oxygen	trawls: 1976/7, 1982 dive: 1984	1, 4
Benthic community	reduced in diversity and numbers off Britannia		1986	5
Common rockweed (*Fucus gardneri*)	entirely absent on 3 km of coastline around Britannia, elevated Cu and Zn content in adjacent areas		1990 (?)	6
Phytoplankton	low productivity in upper basin	likely due to light scattering by silt	1974, 1975	7

Table 4.1. Results of field studies related to effects of AMD discharges to Howe Sound on marine organisms. References cited are: (1) Goyette and Ferguson (1985), (2) Stump et al. (1979), (3) Harbo and Birtwell (1983), (4) Levings (1980), (5) Ellis and Hoover (1990), (6) Dunn et al. (1992), (7) Stockner et al. (1977). Note that the mine closed in 1974.

Bioassays

Organism	Duration	Cu$_{diss.}$ [mg/L]	Observed effect	Water type
Edible mussel (*Mytilus edulis*)	15 days	0.099	30% mortality, byssal thread reduction	Britannia Creek diluted
	15 days	0.163	50% mortality, byssal thread reduction	AMD diluted
Stickleback (*Gasterosteus aculeatus*)	96 hours	1.32*	LC$_{50}$	AMD diluted
Rainbow trout (*Salmo gairdneri*)	96 hours	0.08 and 0.05	100 % mortality	Britannia Creek at townsite
	96 hours	0.03 and 0.05	no lethal effects	Britannia Creek at mouth
Chum salmon (*Onchorhynchus keta*)	96 hours	1.29*	LC$_{50}$	AMD diluted
Chum salmon (*O. keta*) frys	96 hours	0.24	100% mortality	AMD diluted
	25 days	0.25 - 0.26	30 - 40% mortality	AMD diluted
Chinook salmon (*O. tshawitscha*)		0.26	increased Cu contents in guts	AMD diluted
Coho salmon (*O. kisutch*) smolts	30 days	0.013	no mortalities, no increased metallothionein in liver	AMD diluted
Daphnia	96 hours	0.03	EC$_{50}$	Britannia Creek at townsite
	96 hours	0.01	EC$_{50}$	Britannia Creek at mouth

Table 4.2. (continued next page)

Organism	Duration	Cu$_{diss.}$ [mg/L]	Observed effect	Water type
Amphipod (*Anisogammarus conferviculus*)	96 hours	0.075*	no lethal effects	AMD diluted
Brine shrimp (*Artemia salina*)	96 hours	0.74*	LC$_{50}$	AMD diluted
Phosphobacterium (*Phosphobacterium phosphoreum*)	15 min.	0.52*	EC$_{50}$	AMD diluted

Table 4.2. Results of laboratory experiments related to effects of AMD on marine and freshwater organisms. Copper concentrations marked with an asterisk (*) are estimated. Zn concentrations are frequently unknown and have not been included. AMD was generally diluted with seawater to a salinity of 19‰ or more. The creek samples at the townsite and at the mouth had a salinity of less than 9‰ in the Daphnia experiment; for the trout experiment salinity is unknown. LC$_{50}$ denotes the concentration that causes mortality in 50% of the organisms. EC$_{50}$ is a corresponding measure in cases where toxicity is not determined via lethality (e.g. for phosphobacteria it refers to the effective concentration that causes a 50% decrease in light emission). References: Moore (1985) and van Aggelen and Moore (1986). Mussel data are from Lis (1994).

experiments (Harrison et al. 1977), thus phytoplankton in Howe Sound may be less susceptible to high metal concentrations than their counterparts in more pristine estuaries.

Cu and Zn are required micronutrients for phytoplankton and perform essential metabolic functions (Sunda 1994). However, at higher concentrations Cu and Zn may become toxic, as does Cd, which is not thought to be an essential element for phytoplankton. There may be numerous ways for a metal to exert a toxic effect, but experimental evidence suggests that often competition for transport ligands on the cell surface may be involved. For example, the toxicity of Cd to the diatom *Thalassiosira weissflogii* is believed to be the result of reduced Fe uptake due to competition of Cd with Fe for the same surface ligands (Foster and Morel 1982). Antagonistic effects between metals have been observed, such as for Si uptake in *Thalassiosira pseudonana* (Rueter and Morel 1981), where the toxicity of Cu (believed to inhibit Si uptake) is alleviated in

the presence of Zn, presumably again due to competition for a common binding site. The toxicity of acid mine drainage may thus not correspond to the sum of the toxic effects of each metal. In an experiment similar to the one described here, Thomas et al. (1980) determined that in a mixture of ten metals, observed toxic effects could be attributed to the presence of Cu and Hg, while other metals such as Cd and Zn present at the same concentrations did not cause a toxic response.

It is well established that the toxicity of most metals depends on the activity of the free ion rather than on the total concentration (Morel and Morel-Laurens 1983, Campbell 1995). Since the free ion activity is usually not an experimentally accessible parameter in salt water, indirect ways of determining it have been developed. The most successful is probably anodic stripping voltammetry (ASV) combined with chemical speciation calculations. Using this elegant method, Bruland (1989) and Coale and Bruland (1988) were able to demonstrate that in open ocean surface waters, dissolved Zn and Cu are over 98% complexed with strong organic ligands and that the free metal activity is orders of magnitude smaller than was previously thought. The use of ASV in polluted coastal areas has not met with as much success, since the electrode suffers from interferences in the presence of high concentrations of Cu or Cd (van den Berg 1981, Wise et al .1983, Obiols et al. 1988). A new method developed by Davison and Zhang (1994), which operates on the basis of diffusion of labile metals through a permeable gel, is more suitable to the estuarine environment, since it is insensitive to salinity differences and capable of detecting a series of metals over a large range of concentrations simultaneously. With this method, the speciation of Cu in the mixing zone of Britannia Creek was studied. Numerical calculations using the program MINTEQ.A2 were compared with the measured speciation and were used to infer the free cupric ion activity in bioassays in which a natural assemblage of phytoplankton was exposed to acid mine drainage.

Not only do metals exert an effect on phytoplankton by acting as nutrients or toxic agents, but there is also a reciprocal effect of phytoplankton on metals (Sunda 1994).

Scavenging of metals onto biogenic particulate matter and incorporation into phytoplankton cells are considered important mechanisms in the vertical transport of metals in the oceans (Collier and Edmond 1984) and can alter the partitioning of metals between the dissolved and particulate phase. In addition, phytoplankton are known to actively and passively release organic complexing agents, which results in a change in the speciation of dissolved metals (Sunda 1994). The experiment described here presented an opportunity to estimate the involvement of such processes in metal cycling in Howe Sound.

4.2. Methods

4.2.1. Bioassay

A natural assemblage of phytoplankton was collected as a 20 L sample of Howe Sound water at a depth of 2 m off Porteau Cove (49°33.70" N, 123°15.28" W) on March 13, 1996. Salinity and pH of the sample were 20‰ and 7.8, respectively. Bloom conditions were evident from the brown appearance of the water and high turbidity (Secchi disk depth 2 m). The sample was kept dark and brought back to the laboratory, where it was filtered through 200 μm mesh to remove larger grazers. Phosphate (1.98 μM as $NaHPO_4$), silicate (49.8 μM as $Na_2SiO_3 \cdot 9H_2O$) and nitrate (52.3 μM as $NaNO_3$) were added. The sample was divided into four subsamples, whereby one served as a control, while the other three received acid mine drainage from the 4100-portal in a ratio of 1:200, 1:1000, 1:4000 (in the following, the corresponding cultures will be referred to as high, medium and low, respectively). The ratios were chosen to yield Cu concentrations representative of the background, intermediate and extreme levels observed in Britannia Bay (Figure 4.1). Salinity and pH decreases caused by addition of AMD were not measured, but can be calculated to not have exceeded 0.1‰ and 0.1 pH units. The subsamples were further split into 1 L aliquots contained in clear acid-cleaned polypropylene Erlenmeyer flasks. The culture vessels were capped tightly to prevent metal contamination by airborne particles and placed in a circulating bath at 10°C. The cultures were continuously supplied with air from which particles had been removed by passing it through a gas-wash bottle filled with DDW. The air was pumped into the vessels by means of acid-cleaned Teflon tubing connected to a small aquarium pump. A second piece of Teflon tubing stoppered with autoclaved glass wool served to equalize the pressure. The cultures were kept under a 12:12 dark:light cycle at 350 μmol photons $m^{-2} s^{-1}$. In addition to being constantly agitated by the air bubbles, the cultures were

shaken three to four times a day. Chlorophyll a and *in vivo* fluorescence readings were taken daily. On day 1, 3 and 14, additional samples were collected for nutrients, species composition, dissolved and particulate metals, and particulate carbon and nitrogen.
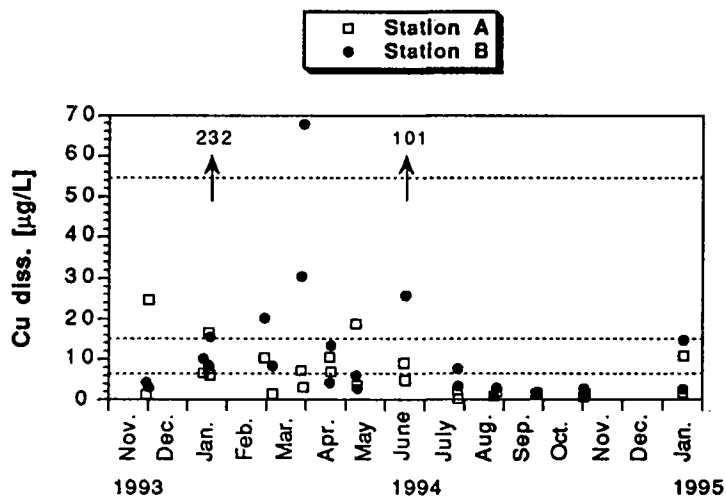
Figure 4.1. Dissolved surface Cu concentrations at Station A and Station B during the period from November 1993 through January 1995. Dashed lines represent initial dissolved Cu concentrations in different phytoplankton culture media made from Howe Sound water to which acid mine drainage had been added. The chosen metal levels simulate background, elevated and extreme metal concentrations in Britannia Bay. The two off-scale values refer to Station B.

Chlorophyll a measurements followed the protocol described in Chapter 2. Nutrient analyses were done spectrophotometrically after Parsons et al. (1989). Species counts on samples preserved by addition of a few drops of Lugol's solution were performed by Rowan Haigh on an inverted microscope (Utermöhl 1958). Dissolved metals were determined by direct injection GFAAS. Particulate metals retained upon 0.4 μm filtration were microwave digested and measured by ICP-MS and GFAAS as described in Chapter 2. Particulate C and N were determined using a CN-analyzer as discussed in Chapter 3.

4.2.2. Speciation

4.2.2.1. Measurement

Change in labile Cu concentration across the mixing zone was determined in a mixing experiment similar to those described in Chapter 3 using a gel diffusion technique developed by Davison and Zhang (1994). Unfiltered Britannia Creek and Howe Sound water samples were mixed to give 2 L aliquots spanning a range of salinities. A gel assembly was suspended in each mixture for a predetermined length of time, as given in Table 4.3. Exposure times were chosen to yield Cu concentrations in the resin layer well above the blanks, but below saturation of the resin. The mixtures were continuously stirred using a magnetic stirrer to ensure homogeneity of the solution and to minimize the thickness of the diffusive boundary layer over the gel. The gel-holder unit was then removed, transferred to a class-100 clean room, rinsed with DDW and taken apart. The resin layer was transferred to an acid-cleaned, weighed Teflon beaker, and any water drops on the resin layer were removed by means of a pipette. The resin was immersed in a known amount (normally about 4 ml) of 2 M environmental grade nitric acid (Anachemia, Vancouver, B.C.) and left to equilibrate for at least two hours. The concentration of Cu in the acid solution was then converted into labile Cu concentrations in the original sample using a calibration curve. This curve was obtained by exposing holders, loaded with gels from the same batch as the one used in the mixing experiments,

Sample	4.1	4.2	4.31	4.32	4.4	4.5	4.61	4.62	4.7	4.8
Exposure [min.]	31	36	41	41	57	89	114	117	192	407
$Cu_{diss.}$ [μg/L]	1530	1430	1280	1220	970	730	480	490	160	2.7

Table 4.3. Exposure times of gel assemblies to mixtures of Britannia Creek water and Howe Sound water, and corresponding concentrations of dissolved Cu.

to solutions of known Cu concentration for different amounts of time. The Cu solutions were made from standard stock solutions in DDW, buffered to a pH of about 6.5 by addition of ammonium acetate, and were verified for their Cu content by ICP-MS. Given the composition of these calibration solutions and the fact that the Cu concentration was always below the saturation concentration for solid Cu hydroxides, it is reasonable to assume $Cu_{diss.} = Cu_{labile}$ in the calibration experiment. A linear relationship between exposure time (Δt) and the ratio of measured metal content of the resin (M_r) to the labile Cu concentration ($[Cu]_{lab.}$, measured as $[Cu]_{diss.}$) was obtained:

$$M_r/[Cu]_{lab.} = -2.9 + 0.0024 \times \Delta t \quad R^2 = 0.99 \tag{4.1}$$

This relationship was used to calculate labile metal concentrations in the mixing experiments from the measured M_r and exposure time. Labile metal can also be calculated via:

$$[M]_{lab} = \frac{M_r}{\Delta t} \frac{\Delta g}{DA} \qquad \text{(Davison and Zhang, 1994)} \tag{4.2}$$

where $[M]_{lab}$ = concentration of labile metal [μg/L]

            M_r = mass of metal in resin eluent [ng]

            Δg = thickness of gel [cm]

            Δt = time of exposure [s]

            D = diffusion coefficient [cm^2 s^{-1}]

            A = exposed surface area of gel [cm^2]

The advantage of using a calibration curve is that it inherently accounts for experimental variables such as temperature-dependence of the diffusion coefficient, incomplete recovery of metals from the resin (Zhang and Davison (1995) correct for this by using an

experimentally derived correction factor), equilibration times between gel and surrounding solution, effect of filter membrane, thickness of the diffusive boundary layer and others.

4.2.2.2. Preparation of Gels

Preparation of gels followed the method described in Davison et al. (1994), with some modifications. For gels, 7.5 mL 1.5 M Tris (tris(hydroxylmethyl)aminomethane), 10.2 mL 40% acrylamide/BIS (a solution containing acrylamide and the crosslinker N,N'-methylene-bis-acrylamide in a ratio of 37.5:1) and 10.7 mL DDW were mixed in a beaker. 300 μL 10% sodium dodecylsulphate, 150 μL 10% ammoniumpersulphate (initiator) and 15 μL TEMED (N,N,N',N'-tetramethylethylenediamine, catalyst) were added and the solution was well stirred (all reagents were purchased from BioRad Laboratories Inc., Mississauga, ON). The gel was then cast between glass plates separated by 0.508 mm thick spacers in a Protean II xi multi-gel casting chamber (BioRad). After the gel had set, it was gently removed from the plates, soaked in 1 M environmental grade HNO_3 for about two hours, rinsed with copious amounts of DDW and stored in fresh DDW until use.

The resin layers were prepared in an analogous fashion. Chelex-100 (100 - 200 mesh, BioRad) was batch-cleaned using several rinses of 2 M HNO_3. The efficiency of cleaning was monitored by GFAAS-analysis of Zn in the wash solution. The pH of the resin was then adjusted to 6.5 using ultrapure ammonia and ammonium acetate buffer (Seastar Chemicals, Sidney B.C.), and the resin again rinsed several times with distilled water. A gel solution was prepared as above, and about an equal volume of Chelex was added. The suspension was then transferred to the casting stand by means of a pipette with a slightly

cut-off tip. Although Davison and Zhang (1994) recommend making the resin layer the thickness of one Chelex bead, in this work resins were cast to 0.38 mm thickness (about three bead diameters). When using thinner spacers, gravitational settling of the Chelex beads was inhibited by friction with the glass casting plates, and the resulting resin gels were very fragile and difficult to handle. After casting, the resin gels were kept in DDW until use.

Custom-made holders were used for deployment of the gels. They consisted of a round acrylic backing plate with an O-ring groove (Figure 4.2). Using a plastic cookie cutter, circles were cut of the resin and gel sheets and placed onto the backing plate. An acid-cleaned cellulose acetate membrane (nominal pore size 0.4 μm) was added on top of the gel layer to prevent fouling of the gel by adhering particles upon deployment. Another acrylic plate was laid on top and fastened to the backing plate by plastic bolts. A round window of 3 cm diameter in the front plate allowed the gel to be exposed to the solution.
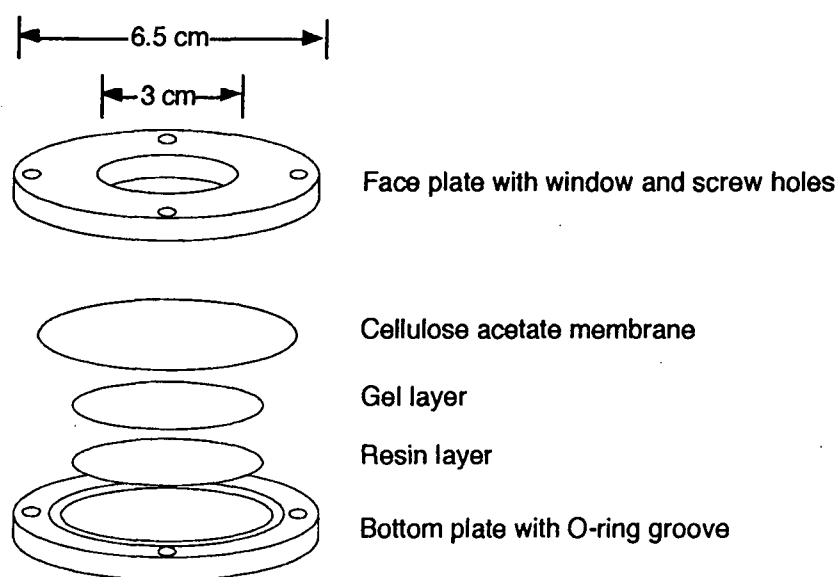
Figure 4.2. Exploded view of gel holder assembly.

4.3. Results

4.3.1. Bioassay

The results of the incubation experiments are summarized in Figure 4.3. The control culture, to which only nutrients, but no acid mine drainage had been added, behaved in a manner typically observed in this kind of experiment. After a short period of adjustment, the cells grew exponentially, shown by a rapid increase in fluorescence and chlorophyll a. Eventually, growth leveled off due to nutrient limitation. At this stage, the availability of nutrients is governed by the remineralization rate of organic matter. The cultures to which AMD had been added at low and medium concentrations essentially followed the same pattern, although with some important differences: their lag phase was longer, and the maximum amount of chlorophyll a produced was smaller. The differences are significant and appear to be directly related to the concentration of acid mine drainage. The culture exposed to high levels of AMD failed to grow at all initially, and only started to recover after eight days. Chlorophyll a and fluorescence at the end of the experiment (day 15) were comparable to the levels found in the other cultures. Low levels of nutrients were found in all cultures as they reached senescence, as measured on day 4 with the control, low and medium cultures, and on day 15 with the high culture: nitrate, silicate and phosphate were < 0.5, < 2.3 and < 0.1 μM, respectively. This compares to initial concentrations (after enrichment) of 66.5, 52.7 and 3.4 μM, respectively.
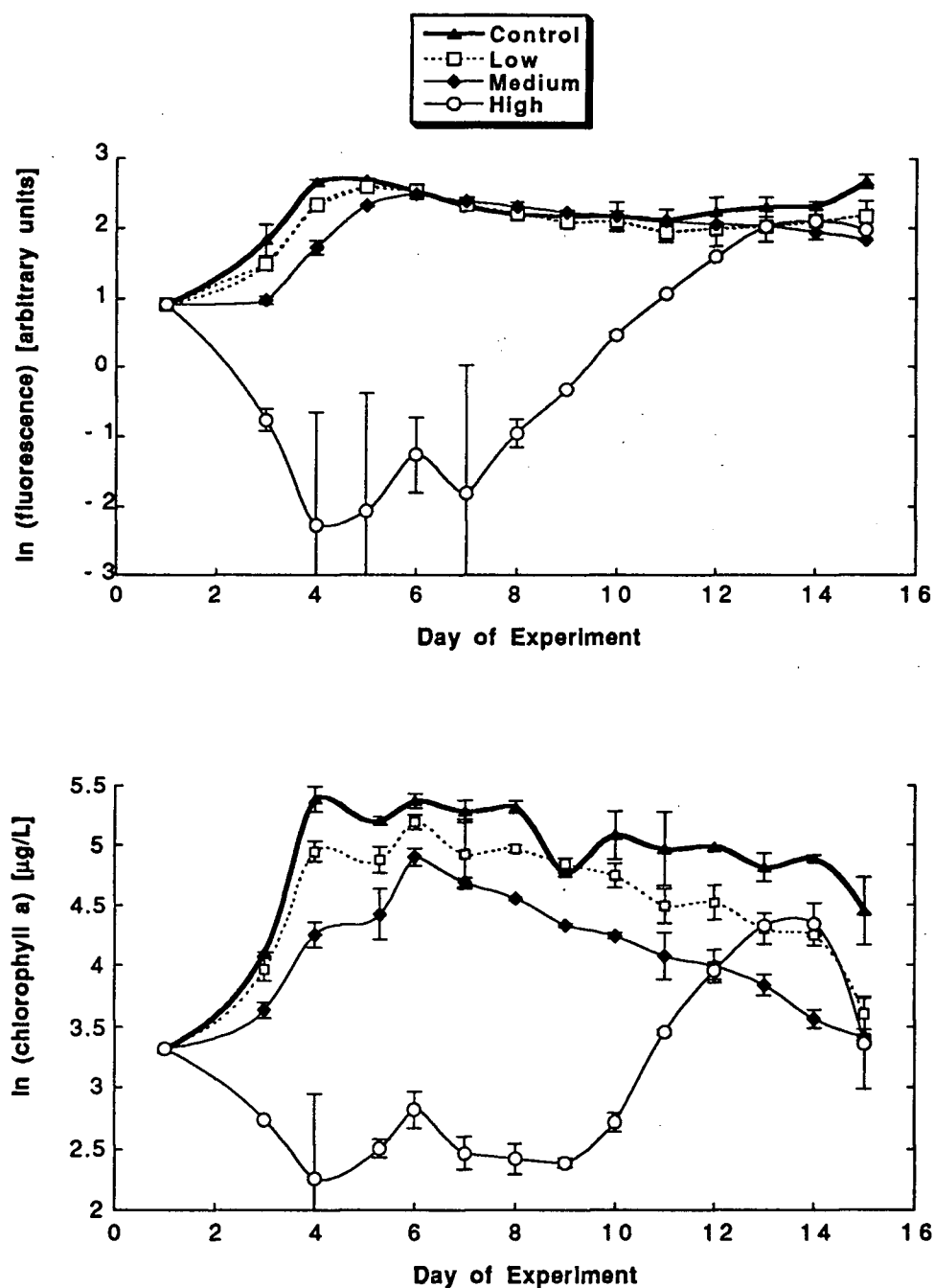
Figure 4.3. *In vivo* fluorescence (top) and chlorophyll a (bottom) in cultures of a natural assemblage of phytoplankton collected in Howe Sound on March 13, 1996. "Low", "Medium" and "High" refer to the concentration of metals from AMD, which was added in a ratio of 1/4000, 1/1000 and 1/200, respectively. The corresponding dissolved Cu concentrations at the beginning of the experiment were 6.4, 15 and 55 µg/L, respectively, while in the control it was 5.6 µg/L. Error bars are one standard deviation of three replicate cultures.
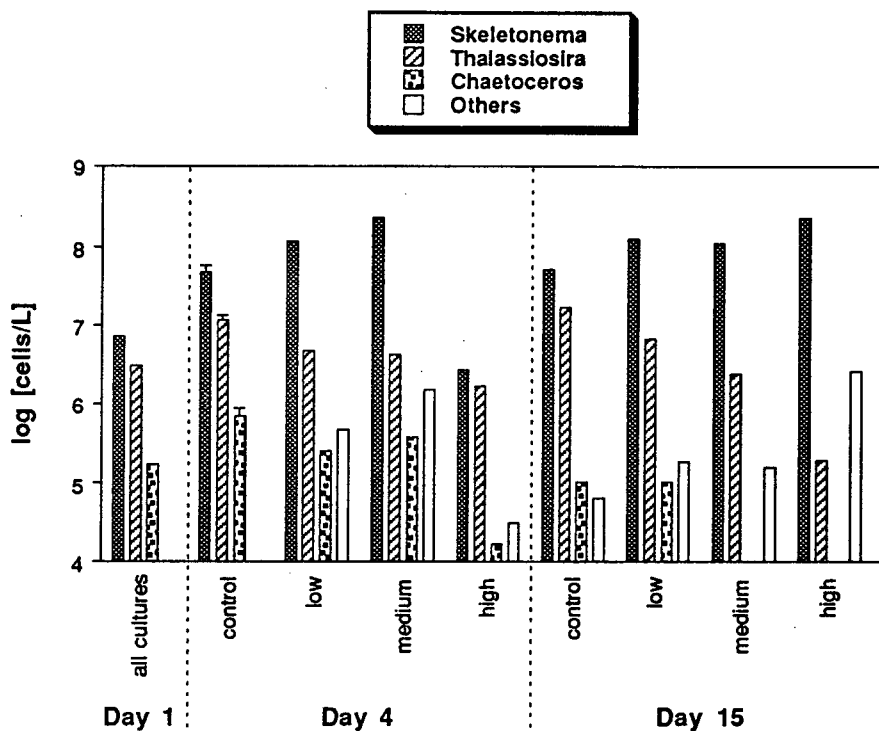
Figure 4.4. Change in species composition of cultures of a natural assemblage of phytoplankton collected in Howe Sound on March 13, 1996. "Low", "Medium" and "High" represent cultures to which AMD had been added (refer to Figure 4.2 for details). Counts were done on the first of each triplicate culture, and with all three replicate cultures with the control on day 4. The error bar in this case represents one standard deviation. Skeletonema were entirely *S. costatum*. *Thalassiosira* species were dominated by *T. nordenskioldii* and *aestivalis*, while *Chaetoceros* species observed were mostly *C. similis* and *debilis*. Other species enumerated included *Pseudo-nitzschia delicatissima*, *Cylindrotheca closterium*, and *Chaetoceros compressus* and *diadema*. Species other than diatoms were marginal or entirely absent. 32 species were counted at the beginning of the experiment, while only six were present on day 15 in the high-AMD culture.

In all cultures, species composition changed during the experiment. The plankton assemblage was initially dominated by *Skeletonema costatum* and *Thalassiosira* spp., and this imbalance shifted towards even more *Skeletonema* as the experiment progressed (Figure 4.4). In all cultures, species diversity decreased over time, and fewer species were observed at higher AMD concentrations. Visual observations on day 4 showed that cells in the medium and high treatments were smaller and formed shorter chains than did the

controls, which may indicate that the former were severely stressed. Since nutrient levels were equally low in the control and the medium treatment, it is likely that the stress factor is the high metal concentration rather than lack of nutrients. Cell numbers in all cultures increased until early senescence and remained high afterwards. The highest cell concentrations were found in the medium treatment on day 4 and in the high treatment on day 15 (Table 4.4). At this stage, the cells were growing under nutrient limitation, which may explain the high C/N ratios.

Dissolved and particulate metal concentrations in the cultures (Figure 4.5) did not change dramatically over the course of the experiment. Interestingly, metal concentrations in the low-AMD culture were only slightly higher than in the control, yet a pronounced difference in the growth of the two treatments was observed, which may be due to differences in dissolved metal speciation. Particulate metal concentrations (Figure 4.5) were generally highest around the time of the bloom (day 4 for control, low and medium, day 15 for high), suggesting a biological control on metal partitioning via uptake by phytoplankton or adsorption onto dead and/or living cells. In the control and

	Control	Low	Medium	High
cells/L	62.5×10^6	125×10^6	239×10^6	234×10^6
chl. a [μg/L]	218 ± 23	140 ± 12	70 ± 7.3	43 ± 26
C [mg C/L]	6.6 ± 0.4	5.4 ± 2.0	5.4 ± 1.2	6.3
N [mg N/L]	0.79 ± 0.03	0.56 ± 0.22	0.66 ± 0.11	0.43
C/N	9.7	11.3	9.7	16.9

Table 4.4. Cell numbers, chlorophyll a, particulate carbon and nitrogen, and C/N ratios in cell cultures around the time of their respective blooms (day 4 for control, low and medium, day 15 for high). Errors represent one standard deviation where available. The expected C/N ratio for phytoplankton (Richards-Redfield ratio) is 6.6. "Low", "Medium" and "High" refer to the concentration of metals from AMD, which was added in a ratio of 1/400, 1/1000 and 1/200, respectively. The corresponding dissolved Cu concentrations at the beginning of the experiment were 6.4, 15 and 55 μg/L, respectively, while in the control it was 5.6 μg/L.

the low-AMD treatment, the mean percentage of total Cu present in particulate form was 24%, almost the same as the mean found in surface samples at Station A in Howe Sound . If biological scavenging is in fact involved in metal partitioning, then higher particulate/dissolved metal ratios are expected in cultures, since cell densities in laboratory cultures are usually higher than in the field. The comparable partitioning of Cu in cultures and in Howe Sound indicates that the increase in particulate Cu around the time of the bloom cannot be unambiguously attributed to biological uptake or scavenging. In contrast, particulate Zn made up 70% and 90% of total Zn on day 4 in the control and low treatments, respectively, much more than the maximum field value of 38%. Similarly, particulate Cd accounted for 30 and 16% of total Cd in the control and low addition cultures, respectively, which compares to field values generally below 5%. Thus, biological scavenging plays an important role in Cd and Zn partitioning in these experiments at low metal concentrations. No field data are available for the case of high metal concentration at high salinity as represented in the cultures with medium and high additions of acid mine drainage, hence the importance of biological scavenging under these conditions cannot be assessed.
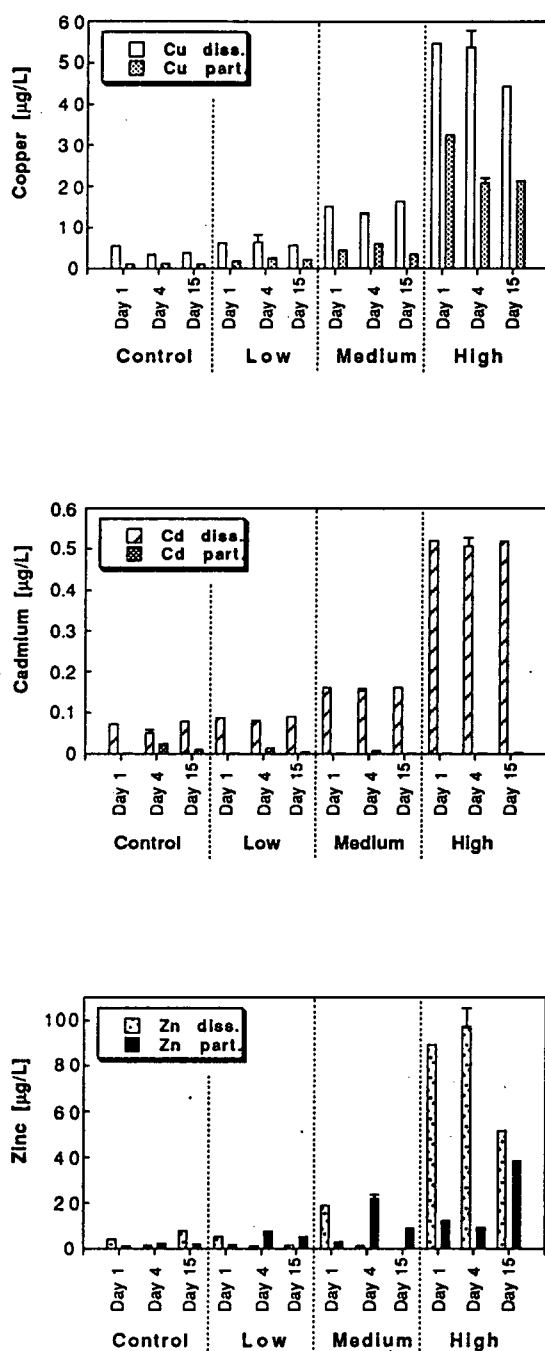
Figure 4.5. Particulate and dissolved concentrations of Cu (top), Cd (center) and Zn (bottom) in culture solutions. "Low", "Medium" and "High" refer to the concentration of metals from AMD, which was added in a ratio of 1/4000, 1/1000 and 1/200, respectively. Error bars represent one standard deviation of the mean of three cultures and were determined on day four only. The decrease in total Cu in the high treatment with time may be due in part to adsorption to vessel walls.

4.3.2. Speciation Measurements in Mixing Experiments

Labile Cu concentrations in the mixing zone were determined in an experiment using several mixtures of Britannia Creek and Howe Sound water (refer to Chapter 3 for details of this mixing experiment). Although it had not been possible to perform the same measurements concurrently with the bioassay, due to logistical problems and time constraints, an estimate of the initial metal speciation in the culture experiment could be obtained. This was achieved by first relating labile Cu in the mixing experiment to computer speciation calculations in the same mixtures, and then hindcasting Cu speciation in the phytoplankton cultures using computer simulations.

4.3.2.1. Speciation Determination using the Diffusive Gel Technique

As implied by its name, the diffusive gel technique (DGT, Davison and Zhang 1994) uses the diffusion of ions across a permeable gel layer to distinguish between labile and non-labile metal species. Free ions and possibly small inorganic or organic complexes can diffuse freely from the bulk solution through the 2 - 5 nm pores of the gel membrane (Davison and Zhang 1994). The membrane is backed by a layer of Chelex-100 resin which complexes free metals. Due to the high stability constant of the Chelex-metal complexes, the dissolved free metal concentration at the inner side of the gel layer is essentially zero, and a concentration gradient across the gel membrane is established. This gradient drives the diffusion of ions across the gel membrane. The technique will measure the concentration of free ions and of metals in complexes that are kinetically and thermodynamically labile enough to dissociate within the time required for diffusion of the complex through the gel. The technique will exclude complexes that are too large to pass through the pores of the gel. However, if they have favourable dissociation kinetics and thermodynamics, they can still contribute to the labile metal pool.

DGT-labile metal concentrations may not relate directly to metal toxicity, since DGT measures a suite of metal species, while toxicity is thought to depend primarily on the free ionic activity. Additionally, lipophilic complexes are likely excluded from the DGT-labile fraction due to their size and complex stability. These compounds can cause toxic effects in phytoplankton (Phinney and Bruland 1994). Although not yet proven, it is possible that in the absence of lipophilic complexes DGT can provide a qualitative measure of toxicity, since under similar experimental conditions the labile concentration of a metal should covary with its free ionic activity.

Gel assemblies were deployed in 2 L polyethylene jars containing unfiltered mixtures of Britannia Creek and Howe Sound water in various proportions. Labile metal is reported only for Cu, since high and variable blanks with Zn and Cd precluded accurate speciation measurements. As shown in Figure 4.6, both dissolved and labile Cu behave non-conservatively during mixing. However, labile Cu decreases much faster than dissolved Cu. Even in the creek sample, there is a significant amount of non-labile dissolved Cu. The percentage of dissolved Cu that is labile quickly decreases to less than 20% (Figure 4.7) and then remains fairly constant as salinity increases (the value at a salinity of 8.75‰ probably has an error of ± 50% due to insufficient exposure time of the gel, see Table 4.3). The decrease in labile metal may be the result of increasing complexation by organic ligands as salinity increases. Since DGT also works on the basis of size exclusion, the decrease could be just as well the result of a change in metal partitioning from truly dissolved to colloidal suspension. While the available data do not permit assessment of the abundance of colloidal Cu, speciation calculations can be used to assess the involvement of organic complexes in Cu speciation. Thus, it may be possible to dismiss organic complexation as being responsible for the decrease in labile Cu.
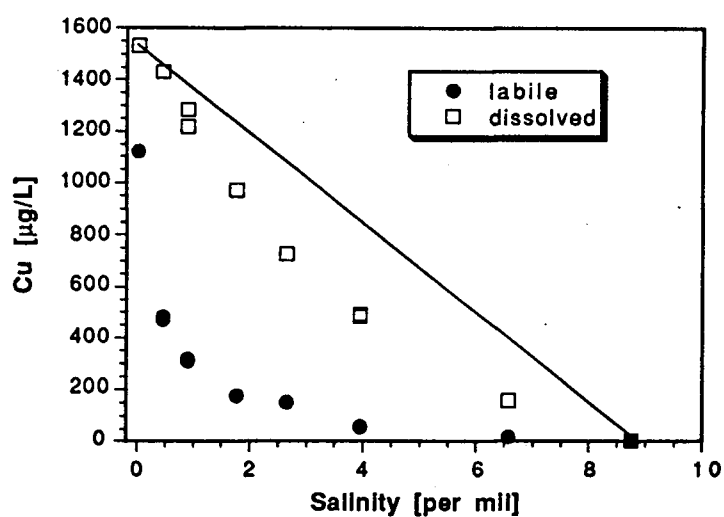
Figure 4.6. Dissolved and labile (as measured by DGT) Cu concentrations in mixtures of unfiltered Britannia Creek water with unfiltered Howe Sound water from the June 1996 experiment. The solid line represents expected dissolved concentrations if Cu were to behave conservatively upon mixing.
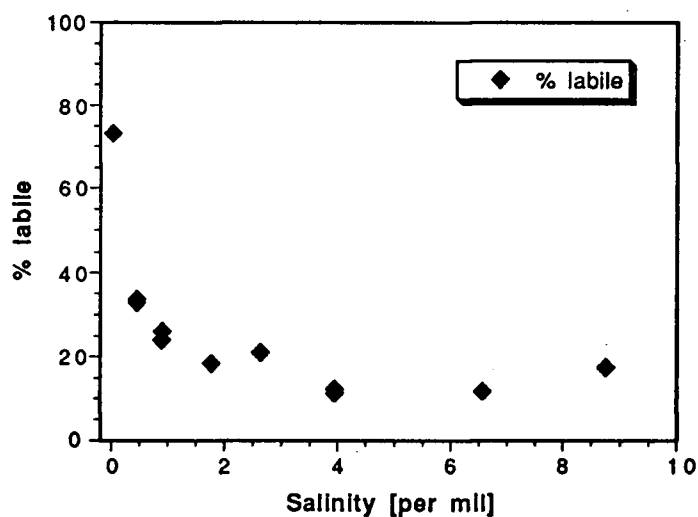
Figure 4.7. Percentage of labile relative to dissolved Cu in the same experiment as in Figure 4.6.

4.3.2.2. Speciation Determination using Model Calculations

The program MINTEQ.A2 (United States Environmental Protection Agency, Athens GA) was used to calculate the distribution of dissolved species of Cu, Cd and Zn in the mixing experiment. Major ion concentrations in Britannia Creek, Squamish River and seawater were estimated according to the sources listed in Table 4.5. These values were used to calculate major ion concentrations in Howe Sound water, assuming it represented a mixture of 35‰ seawater and Squamish River water. Concentrations in the mixtures were determined in an analogous fashion by calculating the fractions of Howe Sound and Britannia Creek water from salinity. Dissolved Cu, Cd and Zn concentrations and pH were measured and are listed in Appendix A.2.3.

Inorganic speciation of dissolved Cu in both freshwater and seawater is dominated by the free ion and by carbonato-complexes (Turner et al. 1981). In freshwater, hydroxo-

	Creek		Squamish		Seawater	
	Conc. [mM]	Ref.	Conc. [mM]	Ref.	Conc. [mM]	Ref.
Na	0.05	1	0.1	2	470	6
K	0.009	1	0.01	5	10	6
Mg	0.07	1	0.5	2	53	6
Ca	0.3	1	0.9	2	10	6
CO_3	0.7	2	0.7	2	2.4	6
SO_4	0.4	1	0.4	2	28	6
Cl	0.2	3	0.2	3	550	6
DOC	1×10^{-3}	4	1×10^{-3}	4	1×10^{-3}	4

Table 4.5. Data used for calculation of Cu, Cd and Zn speciation using the computer code MINTEQ.A2. Concentrations are in mM and refer to the total concentration of the component, not the concentration of a particular species (e.g. $CO_3 = H_2CO_3 + HCO_3^- + CO_3^{2-}$). For assumptions underlying the concentration and binding constants of DOC refer to Section 4.4.3. References are: 1) Price et al. (1995), Britannia Creek at town site; 2) Livingstone (1963), Fraser at New Westminster; 3) Libes (1992); 4) Mantoura et al. (1978); 5) Livingstone (1963), Fraser at Mission; and 6) Stumm and Morgan (1996).

complexes may also be important, depending on the pH. The speciation calculations generally agree with the inorganic speciation predicted by Turner et al. (1981) for fresh- and seawater (Figure 4.8). Minor differences result from the relatively high sulphate concentration in Britannia Creek. Dissolved organic speciation, which was arrived at by assuming DOC was present as a homogeneous class of ligands at a concentration of 1 μM (Section 4.4.3), is greatly influenced by the large decrease in Cu concentrations superimposed on the salinity gradient. At low salinity, most of the organic matter is bound to Cu, but since the concentration of Cu exceeds that of dissolved organic ligands by about 20 times, the effect of organic complexation on Cu speciation is minor. In contrast, at high salinity the concentration of Cu is about 25 times lower than that of organic ligands, and about 45% of the total Cu is bound in organic complexes. Of course the opposite is true for the ligands, which are almost 100% organically complexed at low salinity, while at high salinity only about 2% are associated with Cu. The competition of the major cations Ca and Mg for Cu binding sites is significant at high salinity and is accounted for in the MINTEQ runs. The calculations suggest that organic complexation of Cu in Britannia Bay may be significant. However, because the Cu concentrations are relatively high, the extent of complexation is smaller than in the open ocean where Cu can be > 99% complexed by organic ligands in surface waters (Coale and Bruland 1988, 1990).

Dissolved Cd speciation (Figure 4.8) changes from predominantly free Cd in Britannia Creek to chloro-complexes in seawater, while Zn is present mostly as free aquo ion, in agreement with their expected speciation in natural waters (Turner et al. 1981). With both metals, organic complexation is negligible, which is a result of their generally lower affinity for organic ligands relative to Cu (Buffle 1988, Mantoura et al. 1978) and the high metal concentrations relative to DOC.
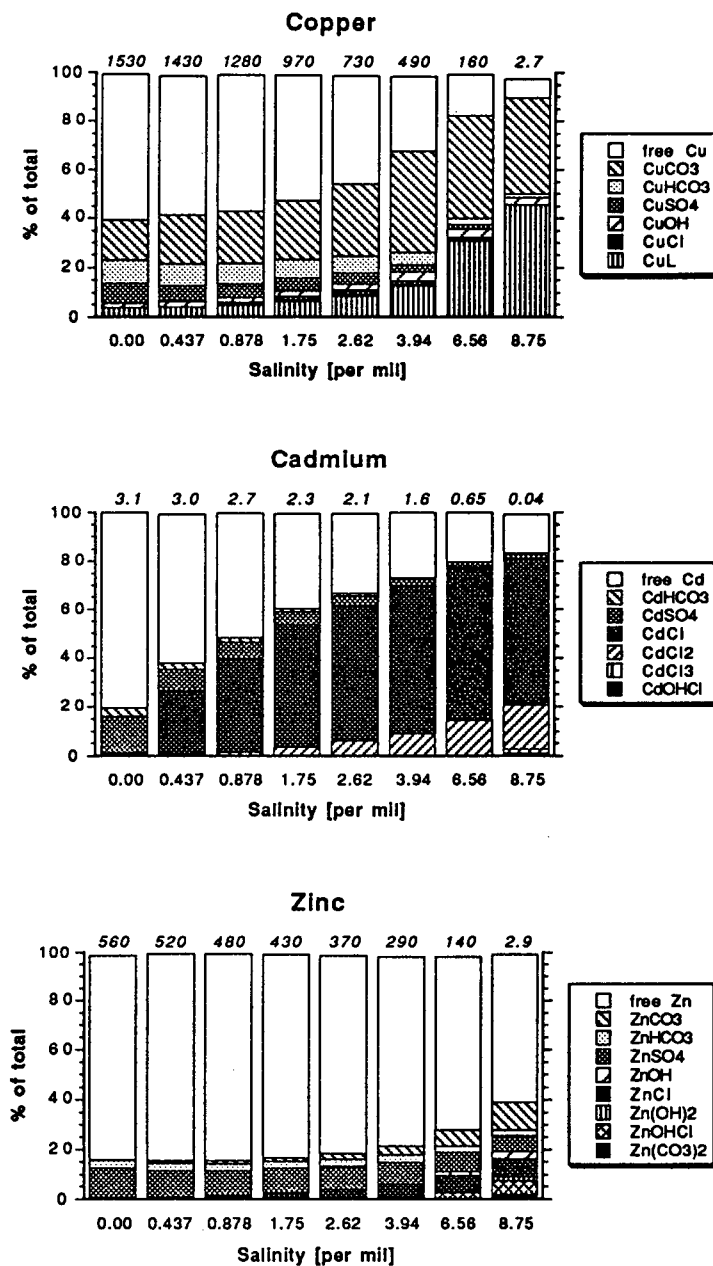
Figure 4.8. Speciation of Cu (top), Cd (center) and Zn (bottom) in mixing experiments calculated using the computer program MINTEQ.A2. Species with abundance less than 1% are not shown. Charges on ionic species have been omitted in the legend, and organic complexes of Cu are shown as "CuL". The respective measured dissolved concentrations (in µg/L) are given above the individual bars.

The calculated organic complexation was used to estimate the labile fraction across the salinity gradient by making the crude assumption that only inorganic Cu species were labile. As shown in Figure 4.9, the calculated labile fraction is only slightly smaller than the measured dissolved (< 0.4 μm) fraction. The calculated labile Cu could be made to agree with the measured Cu by greatly increasing the concentration of organic ligands. However, given the low DOC content of Britannia Creek and its high Cu load, it seems unlikely that organic complexation was grossly underestimated at low salinity. At high salinity (low Cu concentration), agreement could be forced by increasing the ligand concentration and/or the stability constant of the Cu-organic complex. As will be discussed later, the values used (1 μM, log K = 9) are probably overestimates, therefore again it is not likely that organically complexed Cu is greatly underrepresented. Instead, the discrepancy could well be caused by the presence of colloidal forms of Cu, which are excluded from the DGT-measurement, but are included in the total "dissolved" fraction. There is evidence for the presence of colloidal material from other mixing experiments and from SEM-analysis of particulate matter (for details refer to Chapter 3). If Cu, which is supersaturated with respect to $Cu(OH)_2$ in all but the most saline mixtures, is allowed to precipitate in the model calculations, very good agreement between measured and calculated labile concentrations is achieved (Figure 4.9). This is further evidence for a large proportion of 0.4-μm filterable Cu being present in colloidal suspension rather than in true solution.
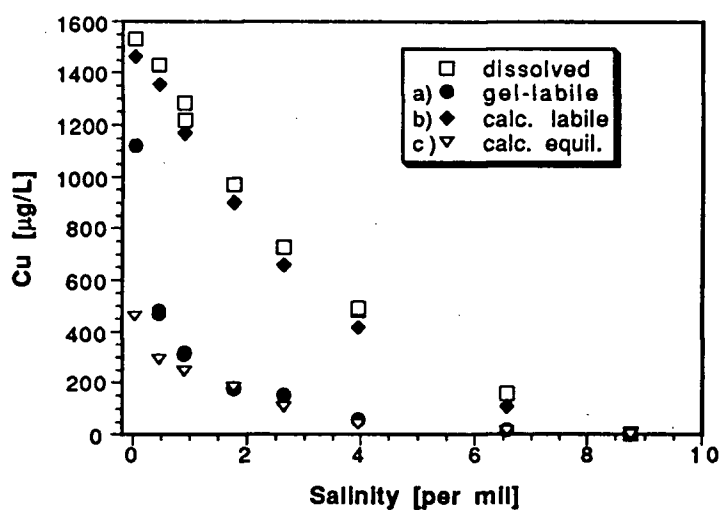
Figure 4.9. Labile Cu concentrations in mixing experiments: a) as measured using the diffusive gel technique ("gel-labile"); b) as calculated using the computer program MINTEQ.A2 without allowing supersaturated phases to precipitate ("calc. labile"); and c) calculated for a solution in equilibrium with $Cu(OH)_2$ ("calc. equil."). Also shown are total dissolved concentrations.

4.4. Discussion

4.4.1. Effect of Metals on Phytoplankton

Metal additions to phytoplankton cultures resulted in an extended lag phase (Figure 4.3), reduced maximum concentration of chlorophyll a (Fig. 4.3), and a shift in species composition (Fig. 4.4). Changes in cell size and appearance were also noted. Other effects commonly observed as a result of metal toxicity include reduced growth rates during logarithmic growth (e.g. Steeman Nielsen and Wium-Andersen 1970, Murphy and Belastock 1980, Sunda and Huntsman 1996), and lower biomass (e.g. Jensen et al. 1976). In the present experiment, neither growth rates (Figure 4.3) nor maximum biomass as inferred from particulate C and N (Table 4.4) were significantly lower in the treatments with metal added compared to the control.

Reduced chlorophyll a concentrations have been reported as a response to high metal concentrations under a variety of experimental conditions, for instance with unicellular laboratory cultures (Hollibaugh et al. 1980), with a natural species assemblage (Thomas et al. 1980) and in microcosm experiments (Spies et al. 1983). Similarly, an extended lag phase has frequently been observed as a response to elevated metal levels, for example in laboratory cultures (Steeman Nielsen and Wium-Andersen 1970), with natural assemblages contained in CEPEX bags (Thomas et al. 1977) and with cultures exposed to a mixture of ten heavy metals in a microcosm experiment (Spies et al. 1983). The initial decrease in chlorophyll a and fluorescence observed in the high AMD treatment and the recovery to levels comparable to the control appear to be typical acclimation responses. Similar effects were reported in cultures of the diatom *Skeletonema costatum* exposed to $HgCl_2$ (Cloutier-Mantha and Harrison 1980) and with the dinoflagellate *Amphidium carterae* at high concentrations of fluoride (Klut et al. 1984). In this latter case, resistance to fluoride even became part of the genetic information, such that an inoculum of the

acclimatized cells grew at the same rate in media containing high levels of fluoride as control cultures did at low levels of fluoride, without going through another acclimation period.

Changes in cell appearance and size are not frequently reported. However, Hollibaugh et al. (1980) observed elongated cells and clumps of daughter cells that had failed to separate after cell division when the diatom *Thalassiosira aestivalis* was exposed to Cu concentrations exceeding 6 µg/L. In the bioassay reported here, cells seemed to be stressed even in the absence of AMD, although the effects were much more pronounced in the cultures where AMD was added, as evident from the small cell size, the short chains and the formation of cell clumps. Nutrient limitation during senescence likely contributed to the observed changes in cell size and appearance.

Shifts in species composition as a response to elevated levels of certain metals have been observed both in freshwater (Deniseger et al. 1990, Gustavson and Wängberg 1995) and saltwater systems (Spies and Parsons 1985, Thomas and Seibert 1977, Thomas et al. 1980). Sensitivity to toxic agents between different species of algae may vary over three orders of magnitude (Cairns et al. 1994). Clearly, more tolerant species will be at less of a disadvantage when exposed to high metal concentrations than sensitive ones. Consequently, they will dominate species composition, and species diversity will decrease, either because sensitive species are outcompeted in their quest for nutrients and light or because they can not grow at all at the metal concentrations encountered. For example, in a natural assemblage grown in CEPEX bags (Thomas et al. 1980) the initially dominant chain-forming diatom Chaetoceros spp. was entirely absent after eight days in a culture exposed to a ten-metal mixture, while it was one of the major species in the control enclosure. Similarly, the metal treatment completely eliminated the pennate diatom *Nitzschia delicatissima*. In contrast, *Thalassiosira* spp. and *Skeletonema costatum*, both chain-forming diatoms, remained abundant. These findings are very similar to the results of the experiment presented here.

The initial species composition was comparable to the assemblage found in Howe Sound in 1974 (Stockner et al. 1977). *Thalassiosira* spp. tolerate low salinity better than *Skeletonema costatum*, while the latter are less affected by low light (Spies and Parsons 1985). Phytoplankton assemblages in Howe Sound may therefore be dominated by either *Skeletonema* or *Thalassiosira* depending on the timing and extent of the Squamish River freshet (Stockner et al. 1977). Also common in Howe Sound are dinoflagellates, *Chaetoceros* spp., and occasionally *Ditylum brightwellii*. (Stockner et al. 1977). While *Chaetoceros* was abundant in the culture experiments, the other species were present only in small numbers. Still, the sample can be regarded as typical for Howe Sound and for a spring bloom in the Strait of Georgia in general (Harrison et al. 1983, R. Haigh, pers. comm.).

The changes in species composition raise the question as to whether the more resistant species could develop some tolerance to high metal levels. In the experiments reported here, an acclimation phenomenon is apparent from the recovery of the cells in the high-AMD treatment after a prolonged lag phase. Development of resistance towards elevated metal concentrations has also been reported by Gustavson and Wängberg (1995) in freshwater and by Thomas et al. (1977) and Harrison et al. (1977) in CEPEX bags. Acclimation appears to involve a physiological change in the algae themselves rather than a detoxification of their environment. Harrison et al. (1977) report that after an initial acclimation period, algae grew normally in water of elevated Cu content. If the cells were removed by filtration and replaced by a culture previously grown at low levels of Cu, the fresh cells showed the same extended lag phase as the adapted culture did initially. Murphy and Belastock (1980) reported that clones of *Skeletonema costatum* and *Thalassiosira pseudonana* from polluted areas were more resistant to organic toxins than clones from more pristine areas. The findings of Klut et al. (1984) with *Amphidium carterae* exposed to fluoride also show that tolerance towards toxic substances may become part of the genetic information. Possibly then tolerant species could have evolved

in Howe Sound, which has been affected by metal inputs for many decades. In view of the highly dynamic environment and the constant water exchange with the Strait of Georgia it seems likely that phytoplankton are constantly advected into and out of Howe Sound, so that they might not be exposed to high metal concentrations for the long periods of time needed to produce genetic changes. Furthermore, the results of the bioassay show a pronounced adverse effect of high metal concentrations on both the species and the community level which clearly negates the presence of a phytoplankton assemblage that is particularly tolerant to extreme levels. With regard to prolonged exposure to moderate metal levels, further experiments would be needed to determine whether phytoplankton from Howe Sound can cope better than their counterparts from more pristine estuaries.

Toxic effects can arise if cells are deprived from obtaining enough of a required nutrient through competition of the toxic metal with the nutrient for a surface binding site. On an intracellular level, toxicity may stem from reduced activity of enzymes through the replacement of an essential metal by a toxic one, from conformational changes in proteins through nonspecific binding of metals to functional groups (e.g. sulfhydryls), or from damaging free radical reactions (e.g. lipid peroxidation) catalyzed by redox-active toxic metals (Sunda 1994). Since metals are present mostly in ionic, lipid-insoluble form (with the notable exception of Hg, but possibly also Cu, Cd and Pb; Phinney and Bruland 1994), attention has focused on transport mechanisms across the cell membrane. In most instances metal uptake seems to proceed via complex formation with a ligand on the cell surface. A porter molecule carries the metal from the binding site through the membrane to the plasma, where it is released (Morel and Hudson 1985). Other models propose that the metal binds directly to the porter molecule (Sigg et al. 1987, Sunda 1991). Although the exact nature of the binding and transport process is not known, the model is widely accepted. It is also compatible with the observation that toxicity of metals is related to the activity of the free ion rather than total metal

concentrations. Competition for surface ligands may explain the toxic effects of Cu, Cd and Zn on phytoplankton. For example, the uptake of the required nutrient Fe by the diatom *Thalassiosira weissflogii* is inhibited in the presence of high concentrations of Cd (Foster and Morel 1982). Addition of a chelating agent resulted in reversal of the toxic effect through reduction of the free Cd activity. Similar antagonistic mechanisms have been proposed for Cu and Mn (Sunda and Huntsman 1983), Cu and Zn (Rueter and Morel 1981) and other metals.

Unlike most laboratory experiments, field assessments of toxicity have to consider effects resulting from the presence of more than one metal. Cd needs to be present at much higher concentrations than Cu to produce comparable toxic effects with the species considered here (Brand et al. 1986, Hollibaugh et al. 1980, Thomas et al. 1980). Since dissolved Cd concentrations in Howe Sound surface waters are typically about two orders of magnitude lower than Cu and Zn, the toxic response observed here is more likely due to the presence of the latter two metals. Braek et al. (1976) reported synergistic effects of Cu and Zn in *Skeletonema costatum* and *Thalassiosira pseudonana*, but these findings have not been confirmed by other workers. Rueter and Morel (1981) demonstrated that it is the ratio of the free Cu to Zn activities that determine their toxic effect, whereby copper toxicity was significantly reduced when zinc concentrations were raised. Jensen et al. (1976) found that individually, Cu was more toxic to *Skeletonema costatum* and *Thalassiosira pseudonana* than Zn at the same concentrations. Of particular importance are the findings of Thomas et al. (1980), because their experimental conditions (origin of organisms, metal concentrations, water properties) are comparable to this study. They exposed a natural assemblage of phytoplankton to several dilutions of a ten-metal mixture. By repeating the experiment with mixtures that contained all metals but Cu or Hg, they were able to show that at comparable concentrations, Cu is by far a more potent toxic agent than Zn. It seems likely that the adverse response to high levels of AMD in the bioassay experiment was caused by Cu rather than by Zn. In fact, the toxicity of Cu

may even have been reduced by the high concentrations of Zn present in acid mine drainage.

4.4.2. Effect of Phytoplankton on Metals

Not only do metals regulate phytoplankton through their roles as nutrients and toxic agents, but phytoplankton also provide a feedback mechanism that can change the speciation of metals and their partitioning between dissolved and particulate forms (Sunda 1994). The cycling of metals in the ocean appears to be closely linked to biological uptake and remineralization processes. Indirect evidence arises from vertical profiles of Cd and Zn, which in the North Pacific show a close correlation with dissolved phosphate and silicate, respectively (Bruland et al. 1978, Bruland 1980). Regulation of metal concentrations by biogenic transport processes has been shown in Hood Canal (Paulson et al. 1993), but in other estuaries was found to be insignificant when compared to abiotic processes (Windom et al. 1991). Using sediment trap data from Funka Bay, Japan, Noriki et al. (1985) were unable to demonstrate clearly a correlation between metal and biogenic particle flux, while in a tank mesocosm (Slauenwhite and Wangersky 1991) the amount of particulate Cd collected in traps increased after a diatom bloom. Topping and Windom (1977) report higher concentrations of Cu in settling material in CEPEX enclosures to which Cu had been added than in the control experiments, and that the particulate Cu was associated mostly with undigested phytoplankton cells that had settled rapidly. In a parallel experiment, Cd associated with particulate matter was also higher in cultures spiked with Cd than in the controls (Kremling et al. 1978); however the fraction of Cd associated with particles made up only a few percent. The results of Collier and Edmond (1984) suggest that much of the metal associated with phytoplankton

(particularly Cu and Cd) may be non-skeletal and therefore subject to rapid remineralization, while the fraction transported to depth via hard parts may be much smaller. Nevertheless, adsorption onto phytoplankton cells may occur, as demonstrated by the efficient removal of Cu, Cd and Zn from solution by freeze-dried cells of the freshwater algae *Chlorella vulgaris* and *Scenedesmus quadricauda* at very high metal to biomass ratios (Harris and Ramelow 1990).

As discussed in Section 4.3.1, the percentage of particulate Cd and Zn around the time of the bloom in the control and low addition cultures was higher than what had been observed in field samples, indicating some association of these metals with biogenic particles. The evidence for Cu is not as clear, although an increase in particulate Cu around the peak of the bloom suggests that biological removal may also occur. While it cannot be resolved whether the metals are actively taken up by the cells or simply adsorb onto them, the evidence demonstrates the importance of phytoplankton for metal partitioning. The results from this experiment can be related to the field, since maximum cell densities exceeded those encountered upon collection of the inoculum only by 4.5 and 8.6 times for control and low-AMD treatment, respectively. Consequently, under bloom conditions metal removal by biogenic particulate matter in Howe Sound may be significant, though this has not been verified in the field.

Phytoplankton may not only change metal partitioning, but also affect dissolved metal speciation. As shown by Coale and Bruland (1988) and Bruland (1989, 1992), dissolved Cu, Cd and Zn in the North Pacific are complexed to a large degree by strong organic ligands of apparent biogenic origin. Similar results have been found for Cu in coastal environments (e.g. Vineyard Sound MA (Anderson et al. 1984), Severn estuary (Apte et al. 1990), Massachusetts Bay (Shine and Wallace 1995), Scheldt estuary (Gerringa et al. 1996), and Southern England (Muller 1996)). Phytoplankton are known to produce ligands that bind Cu and Zn (e.g. McKnight and Morel 1979, Imber et al. 1985, Zhou and Wangersky 1989, Robinson and Brown 1991, Shine and Wallace 1995, Moffett and

Brand 1996). However, as stated by Shine and Wallace (1995), until the ligands are isolated and characterized "it will be difficult to determine whether such ligands are actively produced by phytoplankton in response to metal stress, are a metabolic byproduct of photosynthesis, or [result from] passive release from dead and dying cells". The speciation calculations for the mixing experiment show that complexation of Cu in the mixing zone of Britannia Creek by organic ligands of unknown origin is important, and it is conceivable that organic complexation may also affect the free cupric ion activity in the bioassay experiment, as will be discussed presently. However, in the absence of speciation measurements, we can only speculate whether the cells in the bioassay experiment were able to detoxify the medium via production of chelating agents. At high metal concentrations, the results of Harrison et al. (1977) suggest that acclimation may be a more important mechanism than release of complexing agents for coping with elevated metal levels.

4.4.3. Some Speculations on the Speciation of Metals in Solution

The speciation measurements in the mixing experiments suggest that organic complexation of Cu is not negligible at high salinity. Since Cu may be responsible to a large extent for the toxic effect observed in the bioassay, it is important to estimate its degree of complexation with organic ligands and the resulting activity of free Cu. It should be borne in mind that organically complexed lipophile Cu species could be potentially toxic (Phinney and Bruland 1994). However, since estimates of their abundance in natural systems are lacking at the present time (Phinney and Bruland 1994), it will be assumed in the following discussion that the major influence of organic ligands with regards to toxicity is in reducing free ionic Cu concentrations.

Dissolved organic matter in both the oceans and rivers is composed mostly of refractory material (often referred to as humic compounds) of variable and not well characterized composition (Buffle 1988). Carbohydrates and amino acids usually make up less than 10% of the total DOM, but can comprise as much as 25% (Buffle 1988, Fox 1991). Metal binding by humic compounds is thought to be achieved by hydroxyl- and carboxyl-groups, although amino functions may also play a role (Francois 1990, Midorikawa and Tanoue 1996).

In the central northeast Pacific, Cu was found to be complexed by two ligand classes termed L_1 and L_2 ($logK_1$ = 11.5, log K_2 = 8.5), Coale and Bruland 1988). Cu complexation by ligands of biogenic origin has also been observed in several coastal environments (e.g. Scheldt estuary (Gerringa et al. 1996), Southern England (Muller 1996), Massachussetts Bay (Shine and Wallace 1995), and Chesapeake Bay (Gordon et al. 1996)), and the stability constants reported are often similar to L_2. Ligands isolated were primarily of low weight (< 10,000 Da), contained polysaccharides and proteins (Gordon 1992, Midorikawa and Tanoue 1996, Gordon et al. 1996) and may comprise a large amount of humic substances (Gordon et al. 1996); however complete analysis of their structure has not yet been achieved. It is also unclear what proportion of the total DOM these ligands represent.

There are enormous obstacles to modeling metal complexation by natural organic matter due to the complexity of the ligands, the wide range of binding sites and the changes in the nature of DOM in estuaries. However, by making some crude assumptions, it is possible to obtain a rough estimate of the importance of organic complexation on metal speciation in the bioassay experiment. These are as follows:

1) Cu is complexed solely by humic substances, since they are the dominant component of DOM and have a high affinity for Cu (Buffle 1988).

2) An upper limit for the concentration of humic ligands is assumed at 1 μM, which is close to the value by Mantoura et al. (1978) for organic-rich Lake Celin and is

higher than values reported for L_2 in coastal environments (< 0.25 μM, Anderson et al. 1984, < 0.14 μM, Muller 1996, < 0.25 μM, Gerringa et al. 1996). Additionally, this assumption is an overestimate because it neglects the removal of humic acids during estuarine mixing (Sholkovitz et al. 1978).

3) Cu binding constants of marine and riverine humic matter are similar (Mantoura et al. 1978). The value of log K $\approx$ 9 for marine humic compounds is supported by the similar value of the weak ligand L_2 in both coastal and marine environments.

4) The concentration of the strong Cu binding ligand L_1 in estuarine water is negligible. The only organism that has been found to produce a ligand of this strength is the cyanobacterium *Synechococcus* spp. (Moffett and Brand 1996), which is known to be very sensitive to high Cu concentrations (Brand et al. 1986). Moreover, a ligand of this strength has only been observed in the open ocean (Coale and Bruland 1988), while it has not been reported in coastal investigations (Muller 1996, Gerringa et al. 1996).

Using the major ion concentrations given in Table 4.5 (adjusted for a salinity of 20‰), measured dissolved metal concentrations at the beginning of the experiment (Figure 4.5 and Appendix A.2.6), and 1 μM humic compounds with log K = 4 (Mg, Ca), 9 (Cu), and 5 (Zn, Cd) (Mantoura et al. 1978), it is concluded from speciation calculations that about 25% of Cu is present as organic complexes at the beginning of the incubation. Free cupric ion activities are calculated as 2.6 x 10^{-9}, 3.1 x 10^{-9}, 7.2 x 10^{-9}, and 2.7 x 10^{-8} M for control, low, medium and high treatments, respectively. For comparison, free ionic activities as low as 1.3 x 10^{-10} M and 2.4 x 10^{-11} M have been observed to reduce growth of *Skeletonema costatum* and *Thalassiosira pseudonana*, respectively (Brand et al. 1986). However, the calculated activities in the bioassay experiment cannot be directly related to toxic threshold values, for two reasons. First, the toxicity of Cu is likely lower than what its free ionic activity suggests, because of competition with roughly equimolar concentrations of Zn (Rueter and Morel 1981).

Second, the calculated activities are overestimates, since the medium and high treatments are oversaturated with respect to $Cu(OH)_2$. A better approximation of the free cupric ion activity may be obtained by allowing the solution to equilibrate with $Cu(OH)_2$ (s). As shown in Section 4.3.2.2 for the case of the mixing experiments, this procedure can give good agreement between DGT-labile (potentially bioavailable) and inorganic Cu (which under comparable conditions covaries with the free cupric ion activity). When allowing for precipitation of solid Cu hydroxide, the free ion activity remains 2.6×10^{-9} and 3.1×10^{-9} M for the undersaturated control and low treatments, respectively, but decreases to 6.3×10^{-9} M for medium and high cultures. The identical value for these two treatments despite their different total Cu concentration is a necessary consequence of the solution being in equilibrium with solid $Cu(OH)_2$. The identical free ionic activities suggest comparable toxicity of Cu to phytoplankton in the two treatments, which is in marked contrast to the experimental findings. Perhaps then DGT-labile Cu is not a good indicator of Cu toxicity, for example because colloidal Cu species, which are excluded from the DGT-measurement, may be available to phytoplankton.

In the open ocean phytoplankton may detoxify their medium by producing Cu-binding ligands (Bruland et al. 1991). Whether the organisms in this experiment could have produced enough organic ligands to reduce free copper activity to non-toxic levels can be estimated using the data of Fisher and Fabris (1982). They found that a culture of *Skeletonema costatum* excreted 1.8×10^{-16} moles of Cu complexing ligands per cell and per day during logarithmic growth. During the stationary phase, ligand excretion decreased to 0.57×10^{-16} mol/cell/day. This is over an order of magnitude higher than the 7×10^{-17} mol cell^{-1} day^{-1} found by McKnight and Morel (1979) with *Thalassiosira pseudonana*. Using the maximum cell numbers in Table 4.4, the Fisher and Fabris (1982) value translates to a maximum of 4.4×10^{-8}, 8.7×10^{-8}, 1.7×10^{-7} and 1.7×10^{-7} M over four days for the control, low, medium and high treatments, respectively. Speciation calculations that take this additional pool of organic ligands into account (again using

log K_{Cu} = 9) show that the free cupric ion activity decreases only slightly. Thus the apparent reduction of the toxicity of acid mine drainage to the phytoplankton cultures over time may be have been caused by acclimation rather than by conditioning of the medium, in agreement with the findings of Harrison et al. (1977). However, if excretion of Cu-complexing ligands is a self-defense strategy used by algae, then the production of such compounds is expected to increase under Cu stress. The measurements of Fisher and Fabris (1982) were made at ambient Cu levels and probably represent a lower limit. To answer conclusively whether Cu-stressed cells in an environment such as Howe Sound can produce enough ligands to detoxify their medium, speciation measurements would be needed.

4.5. Conclusions

The results of the bioassay using a natural assemblage of phytoplankton clearly show that even at substantial dilution, acid mine drainage discharged to Britannia Bay can cause detrimental effects, as demonstrated by reduced biomass, species diversity and cell size. Some acclimation seems to occur, but the cells exposed to AMD do not fully recover. Adverse effects are observed at Cu concentrations below 10 μg/L, which is a level frequently exceeded in Britannia Bay, particularly in the vicinity of the mine (Station B, Figure 4.1). Box model calculations (Chapter 3) have shown that even at the upper sill some 10 km down-estuary of the mine, Cu concentrations may reach around 10 μg/L at certain times of the year.

The adverse effects are likely caused by the high concentration of Cu rather than by Zn or Cd. In fact, the high levels of Zn may even reduce Cu toxicity by competition for binding sites on the cell surface. In contrast, the concentration of organic matter is too low to greatly reduce cupric ion activity by complexation with strong organic ligands. The results presented here also suggest that the response of phytoplankton to elevated Cu concentrations may not only be the result of increased free cupric ion activities, but also be due to the bioavailability of colloidal Cu. This in turn means that labile Cu concentrations as measured by the diffusive gel technique may not be a good indicator of Cu toxicity. To resolve this issue, detailed bioassays involving concurrent speciation measurements are needed. This is important since the diffusive gel technique has a great potential for use in estuarine waters, particularly because it is not affected by changes in salinity and is suitable for *in situ* deployment, if desired even over periods of days or weeks for long-term monitoring.

Extrapolation of the results of this bioassay to the environment of Howe Sound is difficult. The dynamic nature of the estuary may result in phytoplankton being advected out of upper Howe Sound, thereby reducing exposure time of these organisms to toxic

metal levels. Further, the concentrations of metals in surface water are not constant, but fluctuate and may go through periods of exceedingly high levels (see Figure 4.1). Additionally, the organisms may be affected by low salinity and reduced light penetration from riverine inputs of freshwater and silt. The timing and size of the spring bloom is important for the productivity of the estuary, since it determines the availability of food for heterotrophic organisms. Low availability of light in spring may delay a bloom and cause it to peak at a time when metal concentrations and silt loading increase. In contrast, an early bloom may precede the maximum in metal discharge (in 1994 between April and June) and the Squamish River freshet (which usually starts in May), and therefore remain unaffected by detrimental metal levels or high silt loadings.

Nevertheless, together with the many observations on a variety of organisms both in the field (Table 4.1) and and in the laboratory (Table 4.2), the results reported here confirm that adverse effects of mine effluent on aquatic organisms do exist. They tend to be most pronounced in the immediate vicinity of the mine, but large areas can be affected, as is evident from the high metal concentrations found in Howe Sound surface waters at sites both close to the mine and 1 km offshore. For organisms under environmental stress, such as phytoplankton (due to low light or low salinity) or heterotrophs (due to low supply of food), the effects of elevated metal concentrations may be particularly severe.

4.6. References

Anderson, D.M., J.S. Lively and R.F. Vaccaro, 1984. Copper complexation during spring phytoplankton blooms in coastal waters. J. Mar. Res. **42**, 677 - 695.

Apte, S.C., M.J. Gardner and J.E. Ravenscroft, 1990. An investigation of copper complexation in the Severn estuary using differential pulse cathodic stripping voltammetry. Mar. Chem. **29**, 63 - 75.

Braek, G.S., A. Jensen and A. Mohus, 1976. Heavy metal tolerance of marine phytoplankton III. Combined effects of copper and zinc ions on cultures of four common species. J. Exp. Mar. Biol. Ecol. **25**, 37 - 50.

Brand, L.E., W.G. Sunda and R.R.L. Guillard, 1986. Reduction of marine phytoplankton reproduction rates by copper and cadmium. J. Exp. Mar. Biol. Ecol. **96**, 225 - 250.

Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. Earth Planet. Sci. Lett. **47**, 176 - 198.

Bruland, K.W., 1989. Complexation of zinc by natural organic ligands in the central North Pacific. Limnol. Oceanogr. **34**, 267 - 283.

Bruland, K.W., 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. Limnol. Oceanogr. **37**, 1008 - 1017.

Bruland, K.H., G.A. Knauer and J.H. Martin, 1978. Cadmium in northeast Pacific waters. Limnol. Oceanogr. **23**, 618 - 625.

Bruland, K.W., J.R. Donat and D.A. Hutchins, 1991. Interactive influence of bioactive trace metals on biological production in oceanic waters. Limnol. Oceanogr. **36**, 1555 - 1577.

Buffle, J., 1988. Complexation reactions in aquatic systems: An analytical approach. Ellis Horwood, Chichester.

Cairns, J., P.V. McCormick and B.R. Niederlehner, 1994. Bioassay and field assessment of pollutant effects. In: Advances in Limnology, vol. 42, L.C. Rai, J.P. Gaur and C.J. Soeder eds., E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 267 - 282.

Campbell, P.G.C., 1995. Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. In: Metal Speciation and Bioavailability in Aquatic Systems, A. Tessier and D. R. Turner eds., Wiley, New York, 45 - 102.

Cloutier-Mantha, L. and P.J. Harrison, 1980. Effects of sublethal concentrations of mercuric chloride on ammonium-limited *Skeletonema costatum*. Mar. Biol. **56**, 219 - 231.

Coale, K.H. and K.W. Bruland, 1988. Copper complexation in the Northeast Pacific. Limnol. Oceanogr. **33**, 1084 - 1101.

Coale, K.H. and K.W. Bruland, 1990. Spatial and temporal variability in copper complexation in the North Pacific. Deep-Sea Res. **47**, 317 - 336.

Collier, R. and J. Edmond, 1984. The trace element geochemistry of marine biogenic particulate matter. Prog. Oceanogr. **13**, 113 - 119.

Davison, W. and H. Zhang, 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature **367**, 546 - 548.

Davison, W., H. Zhang and G.W. Grime, 1994. Performance characteristics of gel probes used for measuring the chemistry of pore waters. Environ. Sci. Technol. **28**, 1623 - 1632.

Deniseger, J., L.J. Erickson, A. Austin, M. Roch and M.J.R. Clark, 1990. The effects of decreasing heavy metal concentrations on the biota of Buttle Lake, Vancouver Island, British Columbia. Water Res. **4**, 403 - 416.

Dunn, C.E., J.B. Percival, G.E.M. Hall and A. Murdoch, 1992. Reconnaissance geochemical studies in the Howe Sound drainage basin. Proceedings of the Howe Sound Environmental Workshop, 1992. Can. Tech. Rep. Fish. Aquat. Sci. **1879**, 89 - 99.

Ellis, D.V. and P.M. Hoover, 1990. Benthos on tailings beds from an abandoned coastal mine. Mar. Poll. Bull. **21**, 477 - 480.

Fisher, N.S. and J.G. Fabris, 1982. Complexation of Cu, Zn and Cd by metabolites excreted from marine diatoms. Mar. Chem. **11**, 245 - 255.

Foster, P.L. and F.M.M. Morel, 1982. Reversal of cadmium toxicity in a diatom: An interaction between cadmium activity and iron. Limnol. Oceanogr. **27**, 745 - 752.

Fox, L.E., 1991. The transport and composition of humic substances in estuaries. In: Organic substances and sediments in water, vol. 1, R. A. Baker ed., Lewis Publishers, Chelsea MI, 129 - 162.

Francois, R., 1990. Marine sedimentary humic substances: structure, genesis and properties. Reviews in Aquatic Sciences **3**, 41 - 80.

Gerringa, L.J.A., T.C.W. Poortvliet and H. Hummel, 1996. Comparison of the chemical speciation of copper in the Oosterschelde and Westerschelde estuaries, The Netherlands. Estuar. Coastal Mar. Sci. **42**, 629 - 643.

Gordon, A., 1992. Isolation of compounds with affinity for copper from seawater using immobilized copper ion affinity chromatography. Mar. Chem. **38**, 1 - 12.

Gordon, A.S., B.J. Dyer, R.A. Kango and J.R. Donat, 1996. Copper ligands isolated from estuarine water by immobilized metal affinity chromatography: temporal variation and partial characterization. Mar. Chem. **53**, 163 - 172.

Goyette, D. and K. Ferguson, 1985. Environmental assessment of the Britannia Mine - Howe Sound. Department of the Environment, Environmental Protection Service Pacific Region, Vancouver.

Gustavson, K. and S.-A. Wängberg, 1995. Tolerance induction and succession in microalgae communities exposed to copper and atrazine. Aquat. Toxicol. **32**, 283 - 302.

Harbo, R.M. and I.K. Birtwell, 1983. Trace metal content data for crustaceans and fishes from Howe Sound, British Columbia. Dept. of Fisheries and Oceans, Field Services Branch, Habitat Protection Division, Water Quality Unit, Vancouver.

Harris, P.O. and G.J. Ramelow, 1990. Binding of metal ions by particulate biomass derived from *Chlorella vulgaris* and *Scenedesmus quadricauda*. Environ. Sci. Technol. **24**, 220 - 228.

Harrison, W.G., R.W. Eppley and E.H. Renger, 1977. Phytoplankton nitrogen metabolism, nitrogen budgets, and observations on copper toxicity: controlled ecosystem pollution experiment. Bull. Mar. Sci. **27**, 44 - 57.

Harrison, P.J., J.D. Fulton, F.J.R. Taylor and T.F. Parsons, 1983. Review of the biological oceanography of the Strait of Georgia: Pelagic environment. Can. J. Fish. Aquat. Sci. **40**, 1064 - 1094.

Hollibaugh, J.T., D.L.R. Seibert and W.H. Thomas, 1980. A comparison of the acute toxicities of ten heavy metals to phytoplankton from Saanich Inlet, B.C., Canada. Estuar. Coastal Mar. Sci. **10**, 93 - 105.

Imber, B.E., M.G. Robinson, A.M. Ortega and J.D. Burton, 1985. Complexation of zinc by exudates of *Skeletonema costatum* grown in culture. Mar. Chem. **16**, 131 - 169.

Jensen, A., B. Rystad and S. Melsom, 1976. Heavy metal tolerance of marine phytoplankton II. Copper tolerance of three species in dialysis and batch cultures. J. Exp. Mar. Biol. Ecol. **22**, 249 - 256.

Kremling, K., J. Piuze, K.v. Bröckel and C.S. Wong, 1978. Studies on the pathways and effects of cadmium in controlled ecosystem enclosures. Mar. Biol. **48**, 1 -10.

Klut, M.E., N.J. Antia and T. Bisalputra, 1984. Some properties of a fluoride-resistant mutant of the marine dinoflagellate *Amphidium carterae*. Phycologia **23**, 301 - 310.

Levings, C.D., 1980. Demersal and benthic communities in Howe Sound basin and their responses to dissolved oxygen deficiency. Can. Tech. Rep. Fish. Aquat. Sci. **951**, 27 - 32.

Libes, S.M., 1992. An introduction to marine biogeochemistry. Wiley, New York, 341.

Lis, S., 1994. The effect of discharge from Britannia Mines and Vancouver wharves on *Mytilus edulis*. B.C. Ministry of Environment, Lands and Parks, Vancouver.

Livingstone, D.A., 1963. Chemical composition of rivers and lakes. In: Data of Geochemistry, 6th ed., U.S. Geological Survey Professional Paper 440-G.

McKnight, D.M. and F.M.M. Morel, 1979. Release of weak and strong copper-complexing agents by algae. Limnol. Oceanogr. **24**, 823 - 827.

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

Midorikawa, T. and E. Tanoue, 1996. Extraction and characterization of organic ligands from oceanic water columns by immobilized metal ion affinity chromatography. Mar. Chem. **52**, 157 - 171.

Moffett, J.W. and L.E. Brand, 1996. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. Limnol. Oceanogr. **41**, 388 - 395.

Moore, B., 1985. (Anaconda Britannia Mines) Copper Beach Estates Ltd. AE-2194 receiving environment survey. B.C. Ministry of Environment, Lands and Parks, Vancouver.

Morel, F.M.M. and N.M.L. Morel-Laurens, 1983. Trace metals and plankton in the oceans: facts and speculations. In: Trace Metals in Seawater, E. A. Boyle, C.S. Wong, K.W. Bruland, J.D. Burton and E.D. Goldberg eds., Plenum Press, New York, 841 - 869.

Morel, F.M.M. and R.J.M. Hudson, 1985. The geobiological cycle of trace elements in aquatic systems: Redfield revisited. In: Chemical Processes in Lakes, W. Stumm ed., Wiley, New York, 251 - 281.

Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. Mar. Chem. **52**, 245 - 268.

Murphy, L.S. and R.A. Belastock, 1980. The effect of environmental origin on the response of marine diatoms to chemical stress. Limnol. Oceanogr. **25**, 160 - 165.

Noriki, S., N. Ishimori, K. Harada and S. Tsunogai, 1985. Removal of trace metals from seawater during a phytoplankton bloom as studied with sediment traps in Funka Bay, Japan. Mar. Chem. **17**, 75 - 89.

Obiols, J., R. Devesa and A. Malet, 1988. Study of the copper-zinc interference in potentiometric stripping analysis. Analyst **113**, 1529 - 1532.

Parsons, T.R., Y. Maita and C.M. Lalli, 1989. A manual of chemical and biological methods for seawater analysis. 2nd ed., Pergamon, Oxford.

Paulson, A.J., H C Curl, Jr. and R.A. Feely, 1993. The biogeochemistry of nutrients and trace metals in Hood Canal, a Puget Sound fjord. Mar. Chem. **43**, 157 - 173.

Phinney, J.T. and K.W. Bruland, 1994. Uptake of lipophilic organic Cu, Cd and Pb complexes in the coastal diatom *Thalassiosira weissflogii*. Environ. Sci. Technol. **28**, 1781 - 1790.

Price, W.A., T. Schwab and N. Hutt, 1995. A reconnaissance study of acid mine drainage at the Britannia mine. B.C. Ministry of Energy, Mines and Petroleum Resources, Victoria, B.C.

Robinson, M.G. and L.N. Brown, 1991. Copper complexation during a bloom of *Gymnodinium sanguineum* Hirasaka (Dynophyceae) measured by ASV. Mar. Chem. **33**, 105 - 118.

Rueter, J.G. and F.M.M. Morel, 1981. The interaction between zinc deficiency and copper toxicity as it affects the silicic acid uptake mechanism in *Thalassiosira pseudonana*. Limnol. Oceanogr. **26**, 67 - 73.

Shine, J.P. and G.T. Wallace, 1995. The formation of surface-active organic complexes of copper in coastal marine waters. Mar. Chem. **51**, 145 - 157.

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

Sigg, L., M. Sturm and D. Kistler, 1987. Vertical transport of heavy metals by settling particles in Lake Zurich. Limnol. Oceanogr. **32**, 112 - 130.

Slauenwhite, D.E. and P.J. Wangersky, 1991. Behaviour of copper and cadmium during a phytoplankton bloom: a mesocosm experiment. Mar. Chem. **32**, 37 - 50.

Spies, A., E.D. Nutbrown and T.R. Parsons, 1983. An experimental approach to estuarine microplankton ecology. Estuar. Coastal Shelf Sci. **17**, 97 - 105.

Spies, A. and T.R. Parsons, 1985. Estuarine microplankton: an experimental approach in combination with field studies. J. Exp. Mar. Biol. Ecol. **92**, 63 - 81.

Steeman Nielsen, E. and S. Wium-Andersen, 1970. Copper ions as poisons in the sea and in fresh water. Mar. Biol. **6**, 93 - 97.

Stockner, J.G., D.D. Cliff and D.B. Buchanan, 1977. Phytoplankton production and distribution in Howe Sound, British Columbia: A coastal marine embayment-fjord under stress. J. Fish. Res. Board Can. **34**, 907 - 917.

Stumm, W.S. and J.J. Morgan, 1996. Aquatic Chemistry. 3rd ed., Wiley, New York.

Stump, I.G., J. Kearney, J.M. D'Auria and J.D. Popham, 1979. Monitoring trace elements in the mussel, *Mytilus edulis* using X-ray energy spectroscopy. Mar. Poll. Bull. **10**, 270 - 274.

Sunda, W.G., 1991. Trace metal interactions with marine phytoplankton. Biol. Oceanogr. **8**, 411 - 442.

Sunda, W.G., 1994. Trace metal/phytoplankton interactions in the sea. In: Chemistry of aquatic systems: Local and global perspectives, G. Bidoglio and W. Stumm eds., ECSC, EEC, EAEC, Brussels and Luxembourg, 213 - 247.

Sunda, W.G. and S.A. Huntsman, 1983. Effect of competitive interaction between manganese and copper on cellular manganese and growth in estuarine and marine species of the diatom *Thalassiosira*. Limnol. Oceanogr. **28**, 924 - 933.

Sunda, W.G. and S.A. Huntsman, 1996. Antagonisms between cadmium and zinc toxicity and manganese limitation in a coastal diatom. Limnol. Oceanogr. **41**, 373 - 387.

Thomas, W.H. and D.L.R. Seibert, 1977. Effects of copper on the dominance and diversity of algae: controlled ecosystem pollution experiment. Bull. Mar. Sci. **27**, 23 - 33.

Thomas, W.H., O. Holm-Hansen, D.L.R. Seibert, F. Azam, R. Hodson and M. Takahashi, 1977. Effects of copper on phytoplankton standing crop and productivity: controlled ecosystem pollution experiment. Bull. Mar. Sci. **27**, 34 - 43.

Thomas, W.H., J.T. Hollibaugh, D.L.R. Seibert and G.T. Wallace, 1980. Toxicity of a mixture of ten metals to phytoplankton. Mar. Ecol. Prog. Ser. **2**, 213 - 220.

Topping, G. and H.L. Windom, 1977. Biological transport of copper at Loch Ewe and Saanich Inlet: controlled ecosystem pollution experiment. Bull. Mar. Sci. **27**, 135 - 141.

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.

Utermöhl, H., 1958. Zur Vervollkommnung der Phytoplankton-Methodik. Int. Ver. Theor. Angew. Limnol. **9**, 1 - 38.

van Aggelen, G. and B. Moore, 1986. (Anaconda Britannia Mines) Copper Beach Estates Ltd. AE-2194 environmental impact assessment 1985/86 update survey. B.C. Ministry of Environment, Lands and Parks, Vancouver.

van den Berg, C.M.G., 1981. Electroanalytical chemistry of seawater. In: Chemical Oceanography **9**, Academic Press, London, 197 - 245.

Windom, H., J. Byrd, R. Smith, Jr., M. Hungspreugs, S. Dharmvanij, W. Thumtrakul and P. Yeats, 1991. Trace metal-nutrient relationships in estuaries. Mar. Chem. **32**, 177 - 194.

Wise, J.A., D.A. Roston and W.R. Heinemann, 1983. The effects of copper-zinc and copper-cadmium intermetallic compounds in different systems used for anodic stripping voltammetry. Anal. Chim. Acta **154**, 95 - 104.

Zhang, H. and W. Davison, 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. Anal. Chem. **67**, 3391 - 3400.

Zhou, X. and P.J. Wangersky, 1989. Changes in copper-complexing organic ligands during spring blooms in the coastal waters of Nova Scotia, Canada. Mar. Ecol. Prog. Ser. **53**, 277 - 284.

CHAPTER 5

OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1. Conclusions and Recommendations

The abandoned mine at Britannia Beach has served in this work as a model site for the study of the behaviour of the transition elements Cu, Cd and Zn during estuarine mixing under contaminated conditions. The unique use of Cd as an indicator for the dilution of acid mine drainage with seawater greatly facilitated interpretation of field data based on the reactant approach. It was shown that the often implied, but rarely verified condition of two end-member mixing in estuaries did not apply to the mixing zone of Britannia Creek due to the presence of the Squamish River as a third end-member, which resulted in high spatial and temporal variability of the salinity of estuarine surface waters. Simultaneous determination of particulate and dissolved metal concentrations proved to be crucial to recognize the problems with the reactant approach and to verify the mass balance in the mixing zone.

While Cd and Zn behaved essentially in a conservative fashion during mixing, Cu was extensively removed. It is proposed that Cu removal occurs predominantly via precipitation of inorganic Cu phases, in addition to complexation by flocculating organic matter and adsorption on iron oxyhydroxides, clay minerals and POM. The different behaviours of Cu and Zn agree with the lower stability of Zn^{2+}-complexes (Irving-Williams series), while the similarity of Zn and Cd reflects their proximity in the periodic table and consequent close chemical relationship.

Removal of Cu in estuaries has often been reported to be controlled by adsorptive processes rather than by precipitation, and even in environments contaminated by acid mine drainage, precipitation of solid Cu phases need not control the removal of Cu, as shown by Johnson (1980). In Britannia Creek particulate iron concentrations are low, both as a result of the composition of the ore as well as of the selective loss of Fe in the upper reaches of the creek. In combination with high Cu concentrations, this leads to the removal of Cu being governed by both precipitation and adsorptive processes rather than

by adsorption alone. This situation may apply to many other mining operations and industrial discharges in coastal environments. The combined effect of precipitation and adsorption reactions under such circumstances could lead to enhanced removal of Cu relative to less polluted estuaries, where Cu is undersaturated with respect to solid phases and only adsorptive processes are important. Generally, this enhanced removal in contaminated environments is a desired effect since it naturally decreases dissolved Cu concentrations that may be toxic to marine organisms.

The removal of Cu is reflected in the Cu content of particles collected in sediment traps, which decreases with distance from the mine. Additional removal of Cu could occur via aggregation of colloidal particles. Both mixing experiments and speciation determinations suggest that Cu may be present to a large degree in colloidal suspension rather than as truly dissolved species. However, it is possible that only Cu-bearing colloidal particles other than Cu hydroxides such as iron oxyhydroxides and clays are subject to aggregation, since upon progressive dilution with seawater, Cu eventually becomes undersaturated with respect to its solid hydroxides, and re-dissolution of the previously formed colloids may occur. In contrast to Cu, Zn and Cd are not extensively removed via flocculation and sedimentation in Howe Sound. Should these metals behave similarly in other polluted estuaries, elevated dissolved concentrations in coastal environments as a result of anthropogenic inputs are to be expected.

The differences in removal rates between Cu and Zn are reflected in their sedimentation pattern. Cu, which is extensively removed during mixing, was found to be enriched in particulate matter collected in sediment traps in the vicinity of the mine. In contrast to Cu, there was no difference in the Zn content of sinking particles at Stations A and B, in agreement with the almost conservative behaviour of Zn. Vertical transport in Britannia Bay is thought to proceed primarily via abiotic processes, given the low abundance of phytoplankton observed in this area during the field period and in previous studies (Stockner et al. 1977). In the more productive lower estuary, however, Zn and Cd

fluxes could be enhanced during phytoplankton blooms, as suggested by their strong association with biogenic particles demonstrated in the culture experiment with endemic phytoplankton species. Cu in contrast appears to be regulated by such processes to a much lesser degree.

Several parameters known to exert some influence on metal removal in other estuaries were found to be of minor importance in Howe Sound. These include salinity, organic complexation and adsorption onto estuarine particles. As pointed out by Morris et al. (1978), salinity-driven processes may set in at salinities < 1 and could therefore depend on the mere presence of a salinity gradient rather than on the final salinity. The small influence of organic matter on metal removal is a consequence of the nature of the drainage basin (steep slopes with little soil cover) combined with the very high metal concentrations. Metal removal also does not appear to be greatly influenced by particles in the seawater end-member, since in mixing experiments removal efficiency was similar with filtered and unfiltered seawater, provided there were particles present in the creek water. The importance of biogenic particles in metal removal remains to be assessed. At low metal concentrations, the bioassay results indicate that scavenging could contribute to metal removal during phytoplankton blooms. In the upper portion of the estuary, phytoplankton blooms are often suppressed by low salinity and light (Stockner et al. 1977), and the resulting small inventory of biogenic particles is likely incapable of greatly reducing dissolved metal concentrations in surface waters.

On the other hand, there are several parameters that do have a major effect on the extent of metal (specifically Cu) removal. Among these are pH, metal content of the creek and presumably abundance of iron oxyhydroxides, although the importance of the latter cannot be quantified. Since all these parameters are strongly influenced by the AMD discharge to the creek, they tend to covary, whereby during periods of high dissolved metal concentrations pH is low and particulate iron concentrations are high.

This results in a strong correlation between the amount of metal removed and dissolved metal concentrations in the creek.

With removal efficiency being predictable, the system is amenable to model simulations. A simple two-layered box model using salinity, creek discharge, Squamish River discharge and creek metal concentrations as input data provided reasonable estimates of surface dissolved metal levels in upper Howe Sound. Not only is this model in conceptual agreement with the dispersion pattern of AMD as inferred from dissolved metal profiles, but it also helps to identify conditions under which estuarine metal concentrations are most likely to reach levels that could be detrimental to marine organisms.

While there is enough evidence from the literature and from unpublished experiments to indicate that organisms are affected by high metal concentrations in the vicinity of the mine, assessment of toxic effects in the remainder of upper Howe Sound is difficult. Metal concentrations in Britannia Bay are extremely variable and may reach levels that have been shown to severely affect growth of phytoplankton. Model calculations suggest that in spring, metal concentrations which were high enough to reduce growth in the phytoplankton bioassay could extend up to ten kilometres down-estuary of the source. However, the stress imposed on phytoplankton by high metal levels may still be small compared to the effects of low salinity and light penetration. Similarly, for surface-dwelling fish such as salmonids it is not known whether they are impacted by high dissolved metal concentrations, whether they actively avoid metal-rich waters or whether they tend to prefer subsurface waters (which happen to contain less metals) because of their higher salinity. There is also a dearth of knowledge on the effects of metal speciation on salmonids and on the importance of upper Howe Sound in their life history, and further studies are certainly needed.

The diffusive gel technique (DGT) shows great promise for speciation measurements due to its insensitivity to salinity and pH changes and due to its capability of

simultaneously determining the speciation of several metals. Gel holder assemblies could be easily deployed on moorings or floats at various locations in Howe Sound and be collected a few hours later, thereby providing a contemporaneous measure of in situ metal speciation at several sites. Vertical profiles and surface transects of metal speciation could easily be obtained. Alternatively, long-term deployment could be envisaged to provide an integrated measure of labile metal concentrations. It would also be very useful to determine whether there is a correlation between the amount of labile metal as measured by DGT and the response of aquatic organisms to elevated metal concentrations. If this were the case, DGT could be used to complement current water-quality guidelines based on a more sensitive parameter than total dissolved concentrations.

With regards to long-term remediation options for the abandoned mine site, it seems worthwhile to investigate ways by which the metal load in the acidic drainage could be reduced. In fact, since Cu loadings to Howe Sound may approach a tonne per day during periods of high discharge, metal recovery should be considered as a means to reduce the operating costs of a future treatment facility, should one be built. The precipitation of metals by H_2S produced by sulphate-reducing bacteria has been shown to be an effective means to reduce metal burdens in mine effluent (Christensen et al. 1996) and could produce a product acceptable by smelters. This process is currently being tested in a pilot experiment on site. The precipitation of ferrite (an iron oxide of the general formula MFe_2O_4, M = any divalent cation) from AMD solutions (Wang et al. 1996), although not yet commercially feasible, may be another interesting option due to the high demand for ferrite in industrial applications.

In the meantime, it may be possible to devise a temporary disposal scheme that would divert AMD from Britannia Creek, decrease metal deposition at the mouth of the creek and along the shore, and reduce the metal burden of the estuarine surface waters. It is strongly advised that implementation of such a scheme be accompanied by extensive

monitoring before, during and after installation in order to be able to relate the effects - beneficial or detrimental - unambiguously to the changes made. The present study provides much of the information needed to decide on an optimal disposal scheme based on sound scientific principles.

5.2. References

Christensen, B., M. Laake and T. Lien, 1996. Treatment of acid mine water by sulfate-reducing bacteria: results from a bench scale experiment. Water Res. **30**, 1617 - 1624.

Johnson, C.A., 1986. The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. Geochim. Cosmochim. Acta **50**, 2433 - 2438.

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**, 680 - 682.

Stockner, J.G., D.D. Cliff and D.B. Buchanan, 1977. Phytoplankton production and distribution in Howe Sound, British Columbia: A coastal marine embayment-fjord under stress. J. Fish. Res. Board Can. **34**, 907 - 917.

Wang, W., Z. Xu and J. Finch, 1996. Fundamental study of an ambient ferrite process in the treatment of acid mine drainage. Environ. Sci. Technol. **30**, 2604 - 2608.

APPENDIX

A.1. Instrumental Parameters

A.1.1. GFAAS

A.1.1.1. Operating Conditions

	Cu	Cd	Zn	Fe	Al
Wavelength [nm]	327.4	228.8	213.9	248.3	396.2
Lamp current [mA]	4	4	5	5	10
Slit width [nm]	0.5	0.5	1.0	0.2	0.5
Slit height	reduced	reduced	reduced	reduced	normal
Graphite tube	platform	platform	platform	platform	partition
Sample volume [mL]	20	20	20	20	20
Measurement time [s]	1	1	1	1	1
Instrument mode	abs.	abs.	abs.	abs.	abs.
Calibration mode	conc.	conc.	conc.	conc.	conc.
Peak measurement mode	area	area	area	area	area

A.1.1.2. Temperature Programs

A.2.1.2.1. Copper

Step	Temperature [°C]	Time [s]	Ar Flow [L/min]
Ramp	300	6	3
Dry	300	40	3
Ramp	1000	3	3
Ash	1000	3	3
Gas Off	1000	1	0
Ramp/Read	2550	0.9	0
Atomize/Read	2550	3.5	0
Purge	2550	1	3
Cool	40	13.3	3

A.1.1.2.2. Cadmium

Step	Temperature [°C]	Time [s]	Ar Flow [L/min]
Ramp	300	8	3
Dry	300	30	3
Ramp	500	5	3
Ash	500	3	3
Gas Off	500	1	0
Ramp/Read	2000	0.8	0
Atomize/Read	2000	2	0
Purge	2000	1	3
Purge	2300	2	3
Cool	40	13	3

A.1.1.2.3. Zinc

Step	Temperature [°C]	Time [s]	Ar Flow [L/min]
Ramp	300	8	3
Dry	300	40	3
Ramp	700	5	3
Ash	700	3	3
Gas Off	700	1	0
Ramp/Read	2000	0.7	0
Atomize/Read	2000	2	0
Purge	2000	1	3
Purge	2300	2	3
Cool	40	12	3

A.1.1.2.4. Iron

Step	Temperature [°C]	Time [s]	Ar Flow [L/min]
Ramp	300	6	3
Dry	300	30	3
Ramp	400	10	3
Ramp/Ash	1500	20	3
Gas Off	1500	1	0
Ramp/Read	2550	0.8	0
Atomize/Read	2550	3	0
Purge	2550	2	3
Cool	40	13	3

A.1.1.2.5. Aluminium

Step	Temperature [°C]	Time [s]	Ar Flow [L/min]
Ramp	85	5	3
Dry	100	20	3
Dry	150	20	3
Ramp	1000	5	3
Ash	1000	1	3
Gas Off	1000	1	0
Ramp/Read	2700	1	0
Atomize/Read	2700	1	0
Purge	2700	2	3
Cool	40	13	3

A.1.2. ICP-MS Operating Conditions

Parameter	Setting (typical values)
RF power [W]	1350
Argon gas flow rate [L/min]:	
Cooling gas	13.7
Auxiliary gas	0.5
Nebulizer gas	1.0
Sampling position [mm above load coil]	13
Sampler cone orifice [mm]	1.0
Skimmer cone orifice [mm]	0.7
Operating pressure [mbar]:	
Interface running pressure	$< 0.1 \times 10^{-4}$
Expansion chamber pressure	2.2 - 2.9
Analyzer pressure	$(2.2 - 2.8) \times 10^{-6}$
Nebulizer type	de Galan V-groove
Data acquisition:	
Signal detection mode	pulse counting: (Cu, Zn) $< 100\ \mu g/L$ analogue: (Fe, Al, Cu, Zn) 100 - 5000 $\mu g/L$
Operating mode	peak jumping
Dwell time [ms]	10.24
Acquisition time [s]	20

A.2. Data Summary

The following tables contain the analytical data for all samples in the order:

1. surface transects
2. vertical profiles
3. mixing experiments
4. Britannia Creek samples from February 1996
5. sediment traps
6. bioassay

For profiles and transects, times are given in Pacific Standard Time. The streamflows for Britannia Creek are estimates based on records at Cheakamus River, while the Squamish River data are measured values. Wind speeds are given as the north-south component of the wind measured at Squamish airport averaged over a period of six hours prior to the beginning of sampling. Positive values indicate wind from the north (downchannel). The coordinates for the various sampling sites are:

Station A (C1)	Britannia offshore	49° 37.93' N	123° 13.79' W
Station B (C2)	Britannia inshore	49° 37.54' N	123° 12.73' W
Station D	Outfall	49° 37.52' N	123° 12.42' W
Station E	Porteau mid-channel	49° 33.70' N	123° 15.28' W
Porteau	Porteau beach	49° 33.12' N	123° 14.70' W
Woodfibre	Woodfibre mid-channel	49°40.10' N	123° 13.00' W

Stations C3 through C10 in transects have no fixed location, instead they were chosen so as to be spread out over the entire mixing zone of Britannia Creek.

"n.m." (not measured) denotes that either no samples were available to determine the corresponding parameter, as is sometimes the case with temperature, pH, dissolved oxygen or chlorophyll a, or that that a sample was collected, but not analyzed, as for example with Cd in vertical profiles. Brackets { } are used where values are unreliable; for pH and dissolved oxygen this is usually due to malfunction of the field probe; for particulate metals it was caused by leakage of the digestion vials. Dissolved ("diss.") and particulate ("part.") metal concentrations are operationally defined as passing or being retained by a 0.4 μm filter, respectively.

A.2.1. Surface Transects

HS 1193 Transect

Date	30/11/93
Time	10:30 - 12:30

Wind [km/h]	0.866
River discharge [m3/s]	104
Creek discharge [m3/s]	3.38

Tides
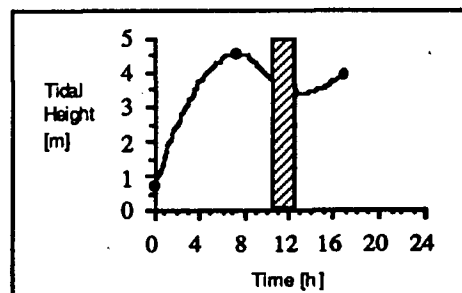
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	n.m.	0	22.7	7.80	n.m.	n.m.
C2	n.m.	0	25.4	7.97	n.m.	n.m.
C3	n.m.	0	25.8	7.75	n.m.	n.m.
C4	n.m.	0	25.1	7.92	n.m.	n.m.
C5	n.m.	0	25.9	7.89	n.m.	n.m.
C6	n.m.	0	26.5	7.93	n.m.	n.m.
C7	n.m.	0	22.9	7.78	n.m.	n.m.
C8	n.m.	0	16.2	8.05	n.m.	n.m.
C9	n.m.	0	2.14	8.29	n.m.	n.m.
C10	n.m.	0	1.86	{8.6}	n.m.	n.m.
C11	n.m.	0	0.00	{8.7}	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	1.28	0.061	3.07	9.77	2.51	0.0145	5.71	103	122
C2	4.43	0.090	7.54	3.79	2.57	0.0036	2.76	53.3	53.4
C3	1.48	0.068	3.21	2.66	2.13	0.0247	2.73	41.0	40.7
C4	2.68	0.076	4.55	13.8	2.49	0.0083	2.99	73.5	76.9
C5	4.45	0.088	10.1	5.30	2.24	0.0050	2.10	46.2	50.1
C6	3.24	0.076	7.47	8.49	1.61	0.0039	1.74	37.6	38
C7	44.5	0.529	103	12.8	42.7	0.0069	9.50	165	234
C8	82.9	1.42	299	6.38	118	0.0089	16.8	222	537
C9	131	1.94	460	11.8	129	0.0134	14.8	256	618
C10	241	2.49	466	84.8	n.m.	n.m.	n.m.	n.m.	n.m.
C11	248	2.48	551	98.6	70.5	0.0121	7.30	216	706

HS 0194 Transect H1

Date	17/1/94
Time	08:45 - 10:15

Wind [km/h]	0
River discharge [m3/s]	98.1
Creek discharge [m3/s]	2.1

Tides
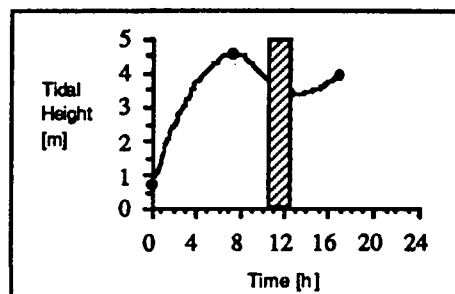
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	6.29	0	11.1	7.99	n.m.	n.m.
C2	6.20	0	7.61	7.84	n.m.	n.m.
C3	6.32	0	8.92	7.77	n.m.	n.m.
C4	6.34	0	4.93	6.79	n.m.	n.m.
C5	6.23	0	2.42	7.33	n.m.	n.m.
C6	6.19	0	2.16	7.18	n.m.	n.m.
C7	6.20	0	2.28	7.41	n.m.	n.m.
C8	6.16	0	1.88	7.19	n.m.	n.m.
C9	6.13	0	1.67	{6.91}	n.m.	n.m.
C10	6.10	0	1.58	{7.08}	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	16.5	0.140	23.7	32.1	3.40	<0.002	0.592	75.5	61.4
C2	233	2.97	451	13.9	22.0	0.0034	1.05	493	543
C3	120	1.79	239	19.3	98.9	0.0038	55.4	204	344
C4	941	5.96	1230	25.3	193	0.0055	7.78	474	763
C5	1300	7.59	1760	256	65.0	0.0035	2.76	434	1090
C6	1350	7.87	1850	256	54.0	0.0036	2.38	421	1200
C7	1350	8.00	1770	272	51.3	0.0038	2.44	471	1470
C8	1460	8.60	1880	268	179	0.0049	15.8	294	583
C9	1540	8.95	1920	295	16.6	0.0032	0.836	523	495
C10	1470	8.90	1750	354	17.2	0.0026	0.779	587	591

HS 0194 Transect L

Date	17/1/94
Time	15:30 - 16:30

Wind [km/h]	-1.24
River discharge [m3/s]	98.1
Creek discharge [m3/s]	2.93

Tides

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	5.03	0	8.98	8.00	n.m.	n.m.
C2	6.43	0	9.21	8.00	n.m.	n.m.
C3	6.53	0	9.46	7.79	n.m.	n.m.
C4	6.57	0	6.97	7.49	n.m.	n.m.
C5	6.56	0	6.85	7.55	n.m.	n.m.
C6	6.58	0	2.15	6.98	n.m.	n.m.
C7	6.58	0	1.93	6.79	n.m.	n.m.
C8	6.56	0	1.59	5.84	n.m.	n.m.
C9	6.55	0	1.59	5.85	n.m.	n.m.
C10		0	1.58	5.95	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	7.76	0.072	15.5	31.6	1.35	<0.002	0.362	78.6	66.5
C2	8.49	0.073	11.6	25.9	1.58	<0.002	0.423	75.0	54.3
C3	19.7	0.135	23.8	25.2	4.19	<0.002	0.843	82.5	74.6
C4	379	3.12	674	41.1	205	0.0067	16.7	410	673
C5	454	3.52	769	34.1	224	0.0065	16.5	374	548
C6	1360	7.39	1670	187	84.8	0.0054	3.98	513	1232
C7	1730	8.49	1590	276	33.7	0.0056	1.71	431	467
C8	1850	9.69	1700	338	17.5	0.0042	1.08	555	473
C9	1910	9.42	1690	334	17.8	0.0039	1.10	586	544
C10	1930	9.61	1710	344	17.4	0.0040	1.14	611	530

HS 0194 Transect H2

Date	18/1/94
Time	09:00 - 10:30

Wind [km/h]	0
River discharge [m3/s]	90
Creek discharge [m3/s]	2.55

Tides

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	5.72	0	6.76	7.96	n.m.	n.m.
C2	5.93	0	6.74	7.63	n.m.	n.m.
C3	5.75	0	5.66	7.46	n.m.	n.m.
C4	5.99	0	4.82	7.10	n.m.	n.m.
C5	6.16	0	4.26	7.11	n.m.	n.m.
C6	6.18	0	2.67	6.80	n.m.	n.m.
C7	6.21	0	1.98	6.22	n.m.	n.m.
C8	6.18	0	1.84	6.06	n.m.	n.m.
C9	6.14	0	1.67	5.43	n.m.	n.m.
C10		0	1.58	5.49	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	6.09	0.055	10.9	46.8	0.791	<0.002	0.289	75.8	57.8
C2	15.4	0.110	19.0	47.5	2.53	<0.002	0.569	81.6	66.5
C3	118	0.901	163	33.9	51.5	0.0032	6.01	169	253
C4	1350	7.25	1580	124	106	0.0045	4.35	431	1078
C5	929	5.84	1080	17.6	205	0.0064	9.76	453	706
C6	1560	9.01	1840	183	74.5	0.0048	3.85	467	1390
C7	1830	10.2	1990	247	31.8	0.0036	1.38	481	973
C8	2020	9.25	1810	322	21.1	0.0034	1.02	555	663
C9	2120	10.4	1840	343	17.9	0.0032	0.946	658	536
C10	2100	10.4	1820	371	16.2	0.0041	1.13	599	468

HS 0294 Transect

Date   1/3/94
Time   12:45 - 14:00

Wind [km/h]   -5.00
River discharge [m3/s]   337
Creek discharge [m3/s]   24.3

Tides
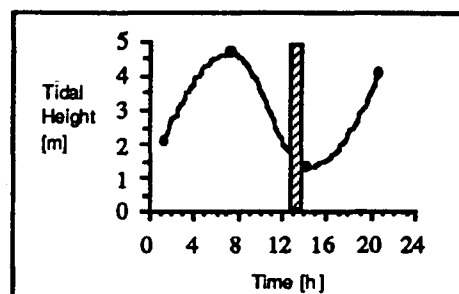
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	n.m.	0	10.1	7.75	n.m.	n.m.
C2	n.m.	0	11.9	7.71	n.m.	n.m.
C3	n.m.	0	12.9	7.77	n.m.	n.m.
C4	n.m.	0	12.8	7.73	n.m.	n.m.
C5	n.m.	0	11.8	7.68	n.m.	n.m.
C6	n.m.	0	10.0	7.62	n.m.	n.m.
C7	n.m.	0	6.75	7.80	n.m.	n.m.
C8	n.m.	0	8.11	7.73	n.m.	n.m.
C9	n.m.	0	6.69	7.64	n.m.	n.m.
C10	n.m.	0	0.03	{8.46}	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	10.3	0.069	8.22	59.8	9.85	0.0043	2.79	473	603
C2	20.1	0.240	30.2	12.6	66.2	0.0368	19.5	1450	4530
C3	13.4	0.102	13.3	24.8	18.1	0.0081	5.01	794	687
C4	16.9	0.139	16.8	7.27	33.6	0.0178	10.6	1510	2200
C5	15.1	0.163	16.7	12.6	23.5	0.0101	6.79	943	1290
C6	16.1	0.243	19.2	80.0	62.7	0.0321	20.0	2910	4400
C7	24.0	0.309	56.6	13.6	107	0.0534	29.7	4500	6050
C8	16.7	0.305	27.2	82.7	60.0	0.0274	17.3	2440	3200
C9	25.0	0.220	38.3	23.6	65.7	0.0322	19.7	3210	4080
C10	177	0.265	64.3	112	92.9	0.122	25.1	2880	3270

HS 0394 Transect

Date   29/3/94
Time   10:30 - 12:30 (?)

Wind [km/h]   3.41   Tides
River discharge [m3/s]   100
Creek discharge [m3/s]   3.66
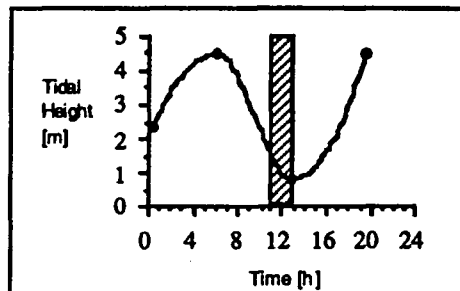
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	9.13	0	27.4	7.80	n.m.	n.m.
C2	8.74	0	26.8	7.86	n.m.	n.m.
C3	8.45	0	26.5	7.75	n.m.	n.m.
C4	8.49	0	26.6	7.77	n.m.	n.m.
C5	8.07	0	24.1	7.75	n.m.	n.m.
C6	7.99	0	22.2	7.71	n.m.	n.m.
C7	7.63	0	16.6	7.97	n.m.	n.m.
C8	7.55	0	14.7	7.94	n.m.	n.m.
C9	6.82	0	1.28	7.63	n.m.	n.m.
C10	6.70	0	1.10	{8.74}	n.m.	n.m.

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	7.31	0.097	10.3	12.0	0.859	<0.002	0.285	38.9	48.4
C2	30.4	0.230	35.9	10.2	6.30	<0.002	1.08	46.1	50.4
C3	39.9	0.301	50.4	10.8	11.9	<0.002	1.85	69.6	72.7
C4	63.2	0.513	94.6	24.0	33.7	0.0027	4.61	135	197
C5	63.6	0.589	99.9	74.8	51.9	0.0044	8.42	471	601
C6	92.8	0.833	153	14.8	126	0.0193	23.7	2000	2840
C7	64.4	0.599	106	7.45	n.m.	n.m.	n.m.	n.m.	n.m.
C8	40.3	0.484	77.1	6.61	76.0	0.0049	7.69	309	396
C9	152	1.15	228	13.0	120	0.0196	6.33	334	322
C10	184	1.34	310	39.6	132	0.0212	6.64	389	413

HS 0494 Transect

Date   20/4/94
Time   11:30 - 13:30

Wind [km/h]   2.74
River discharge [m3/s]   300
Creek discharge [m3/s]   4.87

Tides
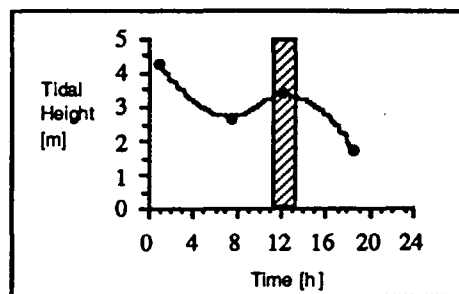
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [μg/L]
C1	11.5	0	20.2	8.24	9.32	0.062
C2	12.1	0	18.0	8.25	8.64	0.019
C3	8.97	0	13.2	8.07	8.64	0.269
C4	9.51	0	11.8	7.98	8.64	0.159
C5	9.38	0	8.91	7.78	8.47	0.227
C6	7.90	0	7.11	7.46	8.55	0.083
C7	7.36	0	2.75	6.95	8.38	0.074
C8	6.83	0	0.34	6.05	8.64	0.038
C9	6.56	0	0.02	5.38	8.21	0.027
C10	7.09	0	0.06	5.57	8.13	0.018

	Cu diss. [μg/L]	Cd diss. [μg/L]	Zn diss. [μg/L]	Fe diss. [μg/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
C1	10.5	0.080	11.7	3.72	2.34	<0.002	0.594	32.8	31.3
C2	4.24	0.053	7.60	3.67	0.626	<0.002	0.444	47.4	54.1
C3	149	1.41	285	9.10	402	0.0134	37.6	435	409
C4	107	0.853	181	14.1	256	0.0091	33.5	290	192
C5	217	1.95	355	11.5	462	0.0132	33.0	500	532
C6	219	1.87	355	13.3	480	0.0132	33.2	527	564
C7	760	2.51	483	20.2	312	0.0082	9.95	641	603
C8	1190	3.33	607	158	58.8	0.0049	1.87	592	702
C9	1360	3.62	577	212	21.3	0.0056	1.04	613	467
C10	1360	3.60	576	242	19.4	0.0064	1.29	586	368

HS 0594 Transect

Date   10/5/94
Time   14:30 - 16:30

Wind [km/h]   -1.95   Tides
River discharge [m3/s]   440
Creek discharge [m3/s]   4.82

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	13.4	0	4.37	7.97	9.15	0.138
C2	11.1	0	4.03	8.01	8.98	0.086
C3	11.5	0	4.10	7.26	8.81	0.086
C4	10.0	0	2.79	6.59	8.47	0.136
C5	10.0	0	3.21	6.74	8.47	0.148
C6	9.38	0	1.40	6.11	8.38	0.057
C7	9.11	0	0.85	5.73	8.47	0.046
C8	8.70	0	0.10	5.20	8.30	0.016
C9	8.70	0	0.05	4.98	8.13	0.039
C10	8.70	0	0.05	4.97	8.13	0.039

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	18.6	0.106	28.4	11.4	11.6	0.0031	2.39	452	573
C2	5.95	0.040	9.30	9.83	2.45	0.0023	1.77	499	770
C3	219	1.14	215	3.76	251	0.0061	7.88	586	842
C4	1440	2.95	596	13.6	274	0.0059	5.22	832	766
C5	1200	2.82	583	11.6	293	0.0057	5.86	825	861
C6	2030	4.04	665	218	82.1	0.0042	1.78	833	784
C7	2450	4.17	790	282	26.3	0.0048	1.09	890	539
C8	2540	4.34	831	321	15.1	0.0042	0.878	963	268
C9	2550	4.39	862	362	13.0	0.0045	0.887	980	188
C10	2580	4.33	879	352	12.1	0.0040	0.736	947	176

HS 0694 Transect

Date   16/6/94

Time   10:30 - 12:30

Wind [km/h]   0

River discharge [m3/s]   260

Creek discharge [m3/s]   2.44

Tides
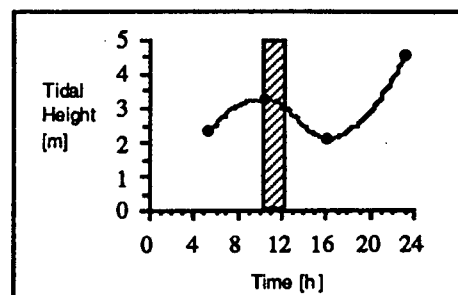
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	12.7	0	3.12	8.16	10.51	0.193
C2	13.0	0	2.09	7.93	10.68	0.171
C3	11.9	0	2.09	7.13	10.17	0.076
C4	10.3	0	1.13	6.13	9.83	0.066
C5	10.3	0	0.94	5.63	10.00	0.046
C6	9.64	0	0.60	5.51	10.00	0.025
C7	9.38	0	0.12	5.01	9.66	0.022
C8	9.64	0	0.11	5.39	9.66	0.016
C9	9.38	0	0.03	4.93	9.91	0.011
C10	9.38	0	0.04	4.87	9.66	0.015

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	9.08	0.045	4.24	103	2.54	<0.002	1.03	214	322
C2	101	0.652	102	16.0	105	0.0048	4.83	367	405
C3	387	1.79	231	2.50	195	0.0063	6.24	458	744
C4	795	2.84	374	25.9	159	0.0057	4.60	498	746
C5	1110	3.59	418	68.8	88.7	0.0042	2.56	487	769
C6	1230	3.76	483	96.6	54.5	0.0034	1.50	451	650
C7	1270	3.75	538	103	23.3	0.0033	0.781	462	496
C8	1230	3.74	541	98.5	31.3	0.0043	1.17	529	597
C9	1220	3.96	553	113	21.8	0.0031	0.711	469	402
C10	1300	3.91	569	102	21.9	0.0032	0.732	494	373

HS 0794 Transect

| Date | 28/7/94 |
| Time | 07:30 - 10:30 |

Wind [km/h]	0.00
River discharge [m3/s]	450
Creek discharge [m3/s]	0.716

Tides

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	15.4	0	3.51	7.53	8.04	0.180
C2	17.2	0	3.32	7.62	7.70	0.158
C3	17.3	0	3.56	7.72	7.53	0.204
C4	16.2	0	1.74	7.12	7.44	0.174
C5	16.0	0	1.33	6.99	7.27	0.244
C6	16.0	0	1.20	6.94	7.10	0.184
C7	15.3	0	0.06	6.15	{2.68}	0.011
C8	15.1	0	0.05	6.12	{2.50}	0.013
C9	15.1	0	0.03	6.11	{2.17}	0.009
C10	15.3	0	0.03	6.13	7.10	0.003

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	0.168	0.010	2.91	38.9	0.562	<0.002	1.03	369	685
C2	3.37	0.031	6.67	31.3	1.74	<0.002	0.779	190	344
C3	1.41	0.021	6.92	18.4	1.37	<0.002	0.978	265	486
C4	309	1.69	323	21.0	122	0.0023	5.44	202	319
C5	396	1.79	380	5.30	135	0.0034	5.79	231	445
C6	420	1.89	390	18.6	119	0.0029	5.24	215	408
C7	841	2.90	691	62.4	48.3	0.0021	1.87	205	481
C8	842	2.96	695	65.4	50.4	0.0020	1.90	193	368
C9	854	3.01	703	71.4	46.3	0.0020	1.84	204	452
C10	847	3.00	690	62.6	50.2	0.0026	1.99	198	420

HS 0894 Transect

Date   24/8/94
Time   08:00 - 10:30

Wind [km/h]   0.63
River discharge [m3/s]   291
Creek discharge [m3/s]   0.296

Tides

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [μg/L]
C1	17.6	0	9.37	8.16	7.87	0.180
C2	18.1	0	7.32	8.12	7.53	0.158
C3	17.6	0	6.82	8.08	7.27	0.204
C4	16.6	0	6.78	8.06	7.36	0.174
C5	13.4	0	2.02	7.33	7.36	0.244
C6	12.6	0	0.61	6.76	7.02	0.184
C7	12.6	0	0.65	6.78	7.02	0.011
C8	12.7	0	0.55	6.68	7.27	0.013
C9	12.7	0	0.54	6.64	7.27	0.009

Station	Cu diss. [μg/L]	Cd diss. [μg/L]	Zn diss. [μg/L]	Fe diss. [μg/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
C1	0.734	0.021	4.58	48.3	0.566	<0.002	0.517	130	210
C2	0.759	0.017	2.36	26.9	0.456	<0.002	0.362	84.0	124
C3	5.92	0.055	7.35	25.1	1.57	<0.002	0.599	105	158
C4	24.2	0.179	24.6	47.5	7.78	<0.002	1.14	87.7	132
C5	129	1.09	185	6.42	80.3	<0.002	4.50	92.4	244
C6	257	1.81	303	3.25	78.6	0.0036	3.27	90.7	352
C7	249	1.69	247	7.45	77.9	0.0043	3.33	85.1	344
C8	255	1.71	287	3.97	74.4	0.0037	2.72	74.3	273
C9	260	1.73	332	7.12	80.2	0.0044	3.27	83.1	293

HS 0994 Transect

Date   27/9/94
Time   09:30 - 12:00

Wind [km/h]   1.42
River discharge [m3/s]   247
Creek discharge [m3/s]   0.304

Tides
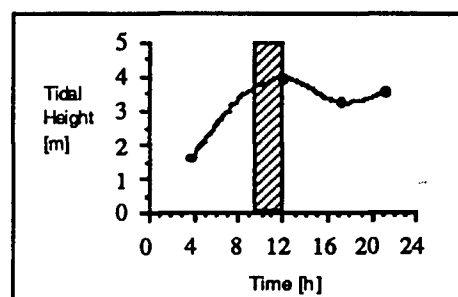
Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]	DOC [mg C/L]
C1	14.7	0	17.0	7.95	9.18	0.699	1.47
C2	13.9	0	13.4	8.02	9.18	0.111	1.53
C3	14.9	0	14.0	8.08	9.18	1.080	3.84
C4	15.0	0	13.2	8.04	8.69	1.880	1.22
C5	13.8	0	2.64	7.80	9.67	0.522	1.78
C6	16.5	0	1.06	7.41	9.08	0.155	1.73
C7	14.1	0	0.38	7.24	10.06	0.128	1.03
C8	13.8	0	0.07	7.14	{0.00}	0.170	0.81
C9	13.7	0	0.03	7.00	{0.21}	0.100	0.55
C10	14.9	0	6.80	8.12	{0.00}	0.989	7.41

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	1.48	0.058	4.88	7.47	0.255	0.00056	0.344	73.8	83.1
C2	1.88	0.049	5.38	5.10	0.455	0.00063	0.643	171	219
C3	3.93	0.080	9.83	11.7	1.10	0.00058	0.759	152	175
C4	6.26	0.105	12.0	8.20	1.59	<0.0005	0.730	124	124
C5	122	1.08	159	2.55	67.4	0.00267	5.01	73.5	182
C6	178	1.44	191	3.36	71.9	0.00381	3.84	63.0	188
C7	294	1.32	205	15.2	64.9	0.00380	3.29	58.5	205
C8	311	1.38	201	18.0	61.3	0.00491	2.81	57.0	186
C9	306	1.42	246	20.8	72.1	0.00650	3.51	60.2	217
C10	93.0	0.809	105	4.98	49.1	0.00168	4.97	82.3	136

HS 1094 Transect

Date	2/11/94
Time	15:00 - 17:00 (?)

Wind [km/h]	1.25
River discharge [m3/s]	102
Creek discharge [m3/s]	1.35

Tides
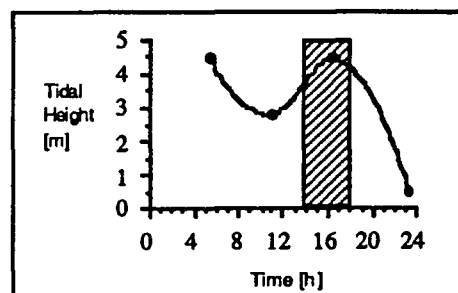
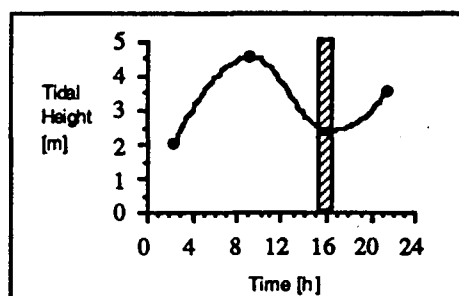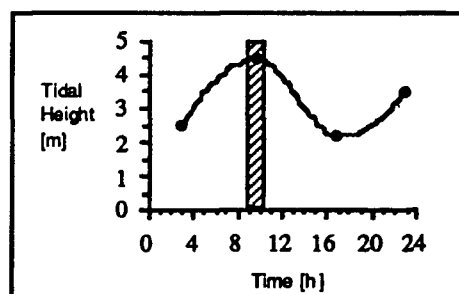| Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1-1	8.44	0	18.8	7.63	6.18	1.72
C2	8.97	0	19.8	7.74	5.97	1.51
C3	9.24	0	21.0	7.86	6.39	2.57
C4	6.42	0	13.6	7.95	7.15	1.61
C5	4.54	0	4.11	7.91	7.81	1.21
C6	3.20	0	1.83	7.62	8.54	0.386
C7	2.93	0	0.43	7.42	8.69	0.242
C8	2.93	0	0.40	7.55	8.68	0.189
C9	2.93	0	0.12	7.42	8.69	0.149
C10	2.80	0	0.02	7.06	8.71	0.174

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1-1	1.41	0.056	6.20	23.0	0.140	<0.002	0.142	48.0	42.9
C1-2	1.12	0.054	6.75	4.47	0.246	<0.002	0.176	55.5	50.1
C1-3	1.42	0.053	3.69	19.2	0.154	<0.002	0.176	53.8	48.6
C2	1.08	0.061	11.4	2.95	0.144	<0.002	0.101	34.8	32.8
C3	5.25	0.086	10.6	5.50	0.531	<0.002	0.207	23.8	18.1
C4	63.1	0.651	87.1	6.13	40.7	<0.002	3.35	58.3	74.6
C5	81.0	0.792	131	6.75	91.6	<0.002	5.57	97.2	215
C6	94.4	0.912	161	3.28	92.2	0.0030	4.09	101	267
C7	142	1.05	188	10.1	84.3	0.0045	3.30	97.7	235
C8	136	1.08	170	6.10	87.4	0.0044	3.36	103	266
C9	145	1.10	177	5.10	87.8	0.0052	3.02	103	296
C10	149	1.17	183	7.00	82.3	0.0063	2.87	96.9	212

HS 0195 Transect

Date	17/1/95
Time	16:00 - 19:00

Wind [km/h]	0.65
River discharge [m3/s]	57.2
Creek discharge [m3/s]	1.50

Tides

Station	Temp. [°C]	Depth [m]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
C1	6.08	0	22.6	7.69	8.92	0.157
C2	5.95	0	21.6	7.61	8.93	0.142
C3	5.53	0	20.9	7.11	8.93	0.113
C4	4.89	0	9.23	7.13	7.80	0.095
C5	4.35	0	3.34	6.42	6.89	0.018
C6	4.31	0	0.90	6.37	6.98	0.019
C7	4.38	0	1.93	6.07	7.87	0.033
C8	4.24	0	0.12	5.00	8.18	0.007
C9	4.24	0	0.12	3.57	8.92	0.013
C10	5.11	0	17.10	7.39	8.91	0.083

	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
C1	1.83	0.061	7.65	4.40	0.436	<0.002	0.126	48.8	26.2
C2	2.52	0.058	3.64	5.72	0.621	0.0024	0.168	53.5	23.8
C3	151	0.758	115	4.25	80.0	0.0037	5.05	127	185
C4	351	1.74	308	10.9	165	0.0032	6.50	210	376
C5	682	2.65	492	8.15	105	0.0030	2.60	233	383
C6	827	2.99	674	10.2	89.8	<0.002	2.29	232	365
C7	774	2.89	653	12.4	115	<0.002	2.92	249	517
C8	965	2.99	685	25.0	35.4	<0.002	0.835	266	500
C9	977	3.10	699	38.9	24.3	<0.002	0.628	296	483
C10	422	2.49	462	3.99	119	<0.002	5.51	168	279

A.2.2. Vertical Profiles

HS 1193 Profiles

Date	2/12/93
Time	8:45 - 11:00

Wind [km/h]	0.00
River discharge [m3/s]	86.9
Creek discharge [m3/s]	2.16

Tides
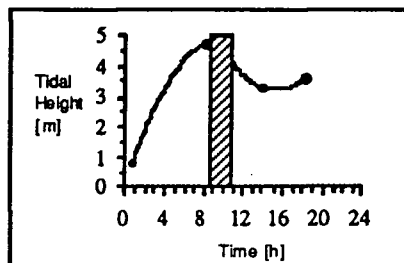
	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	5.98	23.1	7.75	n.m.	n.m.
	5	8.10	28.5	7.84	n.m.	n.m.
	10	8.25	28.6	7.67	n.m.	n.m.
	30	9.38	30.1	7.48	n.m.	n.m.
	50	9.55	30.4	7.62	n.m.	n.m.
	80	9.38	30.5	7.48	n.m.	n.m.
	200	8.65	30.4	7.39	n.m.	n.m.
Station B	0	6.99	24.3	7.60	n.m.	n.m.
	5	8.00	28.3	7.54	n.m.	n.m.
	10	8.24	28.6	7.67	n.m.	n.m.
	30	9.32	30.1	7.64	n.m.	n.m.
	50	9.49	30.4	7.76	n.m.	n.m.
	80	9.40	30.5	7.84	n.m.	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	24.6	0.303	62.4	16.3	6.60	n.m.	1.28	45.0	50.6
	5	0.842	0.062	7.51	2.66	0.047	n.m.	0.088	8.26	8.18
	10	0.657	0.063	5.97	1.99	0.041	n.m.	0.103	9.03	13.6
	30	1.21	0.072	7.44	5.36	1.03	n.m.	0.145	21.8	27.5
	50	0.498	0.064	8.47	3.25	0.061	n.m.	0.111	20.8	30.1
	80	0.624	0.065	5.69	4.82	0.092	n.m.	0.146	23.5	35.1
	200	1.40	0.065	7.02	11.4	0.111	n.m.	0.143	22.3	35.9
Station B	0	3.05	0.078	7.93	9.42	0.450	n.m.	0.192	37.9	45.9
	5	1.01	0.067	4.72	6.27	0.062	n.m.	0.086	14.5	16.4
	10	0.612	0.064	2.71	7.05	0.051	n.m.	0.071	7.67	6.65
	30	1.07	0.077	2.74	12.6	0.083	n.m.	0.136	14.9	13.9
	50	0.619	0.064	1.66	13.4	0.130	n.m.	0.175	18.9	20.5
	80	0.687	0.060	1.95	17.3	0.187	n.m.	0.191	37.5	50.9

HS 0194 Profiles

Date   13/1/94
Time   13:30 - 15:30

Wind [km/h]   0.63
River discharge [m3/s]   125
Creek discharge [m3/s]   4.06

Tides

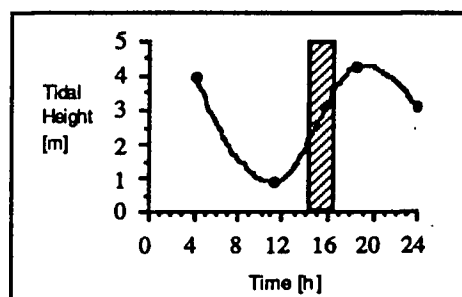|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	n.m.	25.7	7.77	n.m.	n.m.
	5	n.m.	28.1	7.76	n.m.	n.m.
	10	n.m.	29.2	7.66	n.m.	n.m.
	30	n.m.	30.1	7.67	n.m.	n.m.
	50	n.m.	30.5	7.66	n.m.	n.m.
	80	n.m.	30.6	7.65	n.m.	n.m.
	200	n.m.	30.3	7.63	n.m.	n.m.
Station B	0	n.m.	25.4	7.73	n.m.	n.m.
	5	n.m.	27.8	7.75	n.m.	n.m.
	10	n.m.	29.2	7.69	n.m.	n.m.
	30	n.m.	30.2	7.70	n.m.	n.m.
	50	n.m.	30.2	7.76	n.m.	n.m.
	80	n.m.	30.1	7.71	n.m.	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	6.66	0.167	15.4	9.97	1.13	n.m.	0.226	18.9	15.3
	5	0.955	0.079	3.97	9.40	0.071	n.m.	0.113	9.42	10.0
	10	0.861	0.083	2.36	7.60	0.101	n.m.	0.108	14.5	15.2
	30	0.543	0.082	1.93	12.7	0.050	n.m.	0.096	9.05	10.7
	50	0.526	0.083	1.67	11.1	0.059	n.m.	0.115	24.1	23.5
	80	0.653	0.084	1.40	13.0	0.073	n.m.	0.128	14.6	21.8
	200	1.11	0.092	2.01	44.6	0.272	n.m.	0.124	16.7	23.7
Station B	0	10.2	0.188	41.5	16.3	2.89	n.m.	0.475	36.9	28.7
	5	0.789	0.079	3.44	19.5	0.087	n.m.	0.102	9.09	9.58
	10	0.671	0.074	3.27	14.2	0.103	n.m.	0.120	10.8	11.0
	30	0.512	0.064	1.02	9.08	0.050	n.m.	0.092	10.7	11.7
	30	0.494	0.065	1.00	10.0	0.055	n.m.	0.098	16.3	21.6
	30	0.485	0.062	0.954	8.75	0.061	n.m.	0.353	11.3	13.8
	50	0.578	0.067	1.73	9.10	0.096	n.m.	0.124	14.4	18.9
	80	0.452	0.073	1.68	10.1	0.070	n.m.	0.620	19.2	26.3

HS 0294 Profiles

Date   7/3/94
Time   12:00 - 14:30

Wind [km/h]   3.31
River discharge [m3/s]   159
Creek discharge [m3/s]   2.21

Tides

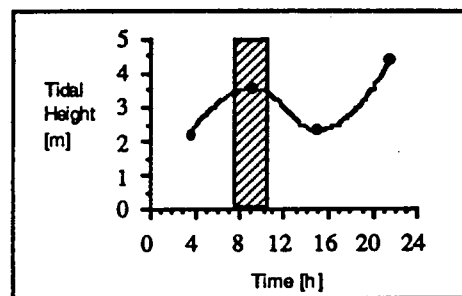|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	7.80	27.1	7.75	n.m.	n.m.
	5	7.99	29.1	7.69	n.m.	n.m.
	10	8.37	29.9	7.66	n.m.	n.m.
	30	8.43	30.1	7.65	n.m.	n.m.
	50	8.68	30.3	7.68	n.m.	n.m.
	80	8.79	30.4	7.6	n.m.	n.m.
	200	9.17	30.6	7.42	n.m.	n.m.
Station B	0	7.88	26.7	7.78	n.m.	n.m.
	5	8.15	29.3	7.69	n.m.	n.m.
	10	8.42	29.9	7.70	n.m.	n.m.
	30	8.46	30.2	7.72	n.m.	n.m.
	50	8.66	30.3	7.74	n.m.	n.m.
	80	8.81	30.4	7.75	n.m.	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	1.54	0.075	4.86	10.4	0.123	n.m.	0.100	30.3	48.2
	5	1.74	0.070	4.97	6.03	0.077	n.m.	0.098	20.0	30.6
	10	1.74	0.070	5.02	6.00	0.090	n.m.	0.129	15.4	23.6
	30	0.90	0.070	3.71	5.09	0.017	n.m.	0.072	12.5	19.1
	50	1.93	0.073	5.81	5.38	0.170	n.m.	0.111	14.3	21.9
	80	1.42	0.070	9.91	4.82	0.050	n.m.	0.090	23.8	38.7
	200	2.12	0.072	12.8	14.0	0.177	n.m.	0.117	64.5	35.3
Station B	0	8.41	0.106	14.1	4.78	0.523	n.m.	0.155	33.0	52.3
	5	5.97	0.157	19.4	5.20	0.769	n.m.	0.271	31.4	43.4
	10	0.993	0.069	1.69	2.91	0.102	n.m.	0.123	16.8	26.9
	30	1.06	0.069	0.976	4.37	0.304	n.m.	0.083	21.4	30.8
	50	{0.33}	{0.001}	{0.612}	{0.129}	{0.02}	n.m.	{0.011}	{1.9}	{1.9}
	80	3.83	0.102	9.94	8.14	0.418	n.m.	0.199	21.8	27.0

HS 0394 Profiles

Date   31/3/94
Time   09:30 - 12:30

Wind [km/h]   2.35
River discharge [m3/s]   145
Creek discharge [m3/s]   4.18

Tides

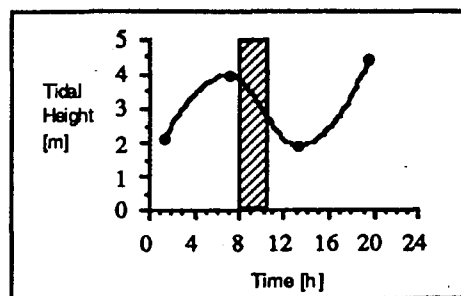|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	8.89	16.0	8.26	n.m.	n.m.
	5	9.43	27.2	8.34	n.m.	n.m.
	10	8.31	28.2	7.96	n.m.	n.m.
	30	8.20	29.8	8.10	n.m.	n.m.
	50	8.35	30.0	8.12	n.m.	n.m.
	80	8.77	30.3	7.96	n.m.	n.m.
	200	9.20	30.5	7.62	n.m.	n.m.
Station B	0	8.46	14.0	8.23	n.m.	n.m.
	5	8.80	27.8	8.25	n.m.	n.m.
	10	8.39	28.2	8.19	n.m.	n.m.
	30	8.85	29.8	8.24	n.m.	n.m.
	50	8.28	30.0	7.98	n.m.	n.m.
	80	8.71	28.5	8.00	n.m.	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	3.01	0.053	2.31	30.8	{0.597}	n.m.	{0.891}	{212}	{314}
	5	1.65	0.075	1.67	2.26	0.282	n.m.	1.05	32.2	39.3
	10	1.60	0.075	1.90	5.30	0.145	n.m.	0.247	25.2	29.2
	30	1.93	0.073	1.61	4.38	0.225	n.m.	0.397	34.7	40.8
	50	1.41	0.075	1.92	9.05	0.244	n.m.	0.352	30.4	35.7
	80	1.79	0.077	3.14	6.87	0.321	n.m.	0.245	24.7	30.5
	200	0.75	0.070	1.56	5.51	0.162	n.m.	0.101	17.6	27.3
Station B	0	67.9	0.759	58.1	29.6	49.1	n.m.	7.00	112	96.5
	5	2.83	0.075	2.09	4.17	0.409	n.m.	0.766	29.6	32.8
	10	2.05	0.076	1.56	4.04	0.208	n.m.	0.281	19.3	22.5
	30	1.92	0.077	1.67	8.41	0.237	n.m.	0.379	19.1	20.7
	50	0.71	0.081	1.01	7.80	0.035	n.m.	0.083	13.4	19.2
	80	1.06	0.073	1.01	12.8	0.141	n.m.	0.162	30.8	45.4

HS 0494 Profiles

Date   21/4/94
Time   09:00 - 11:30

Wind [km/h]   0.00
River discharge [m3/s]   280
Creek discharge [m3/s]   5.33

Tides

	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	9.49	5.39	7.99	8.6	0.327
	5	9.74	25.4	8.20	9.2	0.675
	10	8.61	28.5	8.17	10.3	0.414
	30	8.19	29.8	7.72	8.6	n.m.
	50	8.24	30.0	7.69	8.0	n.m.
	80	8.62	30.3	7.67	8.1	n.m.
	200	9.19	30.5	7.42	5.1	n.m.
Station B	0	9.53	5.59	7.86	n.m.	0.218
	5	10.4	24.0	8.19	10.2	0.378
	10	8.95	27.7	8.20	8.4	0.369
	30	8.20	29.7	7.88	7.4	n.m.
	50	8.26	29.9	7.76	7.6	n.m.
	80	8.66	30.3	7.71	5.5	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	6.84	0.056	4.00	26.6	2.99	n.m.	1.44	286	503
	5	6.11	0.072	4.02	4.00	1.23	n.m.	0.786	81.5	135
	10	2.78	0.065	1.94	3.26	0.238	n.m.	0.234	28.2	30.8
	30	5.31	0.106	8.21	3.04	0.377	n.m.	0.356	26.0	22.9
	50	4.32	0.131	7.81	3.41	0.543	n.m.	0.228	21.5	15.7
	80	4.04	0.105	6.34	2.48	0.567	n.m.	0.323	22.2	20.0
	200	0.575	0.070	3.71	4.40	0.108	n.m.	0.082	20.3	16.8
Station B	0	13.3	0.083	9.23	12.6	6.104	n.m.	1.85	272	434
	5	3.30	0.074	2.82	2.36	0.307	n.m.	0.310	27.7	29.8
	10	3.07	0.072	1.77	3.64	0.424	n.m.	0.528	47.0	71.7
	30	22.0	0.225	29.8	5.37	3.86	n.m.	1.02	33.0	33.9
	50	30.9	0.305	43.9	4.79	5.26	n.m.	1.34	32.5	40.8
	80	3.39	0.068	2.93	9.97	0.303	n.m.	0.193	28.6	36.0

HS 0594 Profiles

Date   11/5/94
Time   14:45 - 18:30

Wind [km/h]   -7.38   Tides
River discharge [m3/s]   420
Creek discharge [m3/s]   5.19

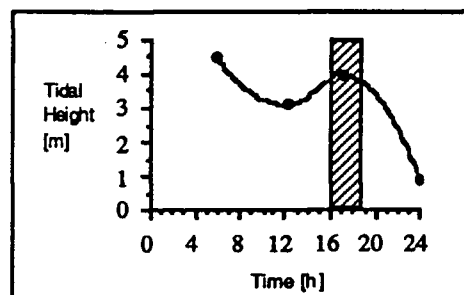|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	11.4	6.50	8.50	9.23	0.345
	5	11.9	22.0	8.10	n.m.	0.566
	10	9.76	26.9	8.16	6.08	1.12
	30	8.31	29.5	8.11	7.27	n.m.
	50	8.20	29.2	8.01	7.78	n.m.
	80	8.64	30.2	7.89	7.27	n.m.
	200	9.17	30.5	7.32	5.66	n.m.
Station B	0	12.0	3.20	8.48	7.95	0.151
	5	12.7	16.5	8.38	4.13	0.579
	10	10.9	25.2	8.03	n.m.	0.988
	30	8.44	29.0	8.08	7.44	n.m.
	50	8.33	29.7	8.07	7.02	n.m.
	80	8.36	30.0	8.03	6.25	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	3.49	0.038	2.05	29.4	1.47	n.m.	1.55	341	538
	5	4.21	0.071	2.55	10.1	0.457	n.m.	0.812	144	250
	10	2.41	0.074	2.54	2.64	0.232	n.m.	0.451	33.0	55.5
	30	3.19	0.077	2.41	6.42	0.277	n.m.	0.400	50.0	82.5
	50	4.70	0.093	6.21	5.08	0.516	n.m.	0.422	32.2	53.9
	80	3.41	0.085	6.39	10.5	0.326	n.m.	0.288	29.6	48.4
	200	0.882	0.070	2.03	5.37	0.070	n.m.	0.074	7.29	12.0
Station B	0	2.82	0.039	3.08	24.2	0.993	n.m.	1.18	288	433
	5	1.80	0.058	3.07	2.25	0.448	n.m.	0.937	110	182
	10	3.13	0.078	4.04	2.34	{0.155}	n.m.	{0.252}	{12.7}	{27.8}
	30	8.76	0.113	9.57	3.44	0.850	n.m.	0.595	54.8	103
	50	4.01	0.075	2.89	7.17	0.515	n.m.	0.415	56.8	108
	80	3.56	0.076	2.63	7.63	{0.408}	n.m.	{0.352}	{42.7}	{77.8}

HS 0694 Profiles

Date	17/6/94
Time	10:00 - 14:00

Wind [km/h]	0.00	
River discharge [m3/s]	300	
Creek discharge [m3/s]	2.27	

Tides
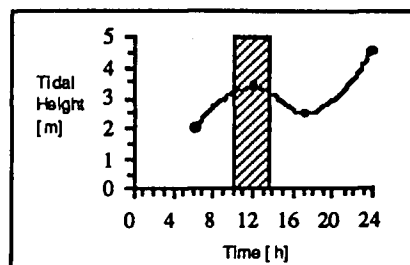
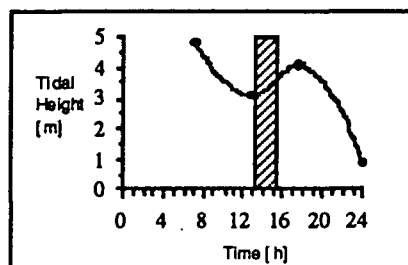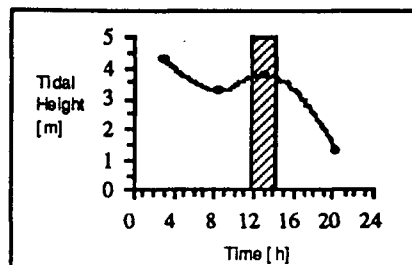|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	12.0	3.56	8.07	9.49	0.263
	5	11.2	24.7	7.86	7.36	0.113
	10	10.0	27.0	7.75	6.59	0.037
	30	8.57	29.4	7.70	5.15	n.m.
	50	8.31	29.6	7.67	4.47	n.m.
	80	8.46	30.1	7.60	4.38	n.m.
	200	9.16	30.5	7.51	2.93	0.025
Station B	0	14.1	3.59	8.50	9.23	0.024
	5	11.2	25.3	7.88	6.93	0.125
	10	9.97	27.1	7.84	6.51	0.059
	30	8.53	29.3	7.77	5.32	n.m.
	50	8.43	29.5	7.73	5.23	n.m.
	80	8.40	30.0	7.76	4.21	n.m.
Woodfibre	0-1	12.9	1.63	8.80	9.83	0.108
	0-2	n.m.	n.m.	n.m.	n.m.	0.121
	0-3	n.m.	n.m.	n.m.	n.m.	0.978
Porteau	0-1	14.1	2.44	8.11	9.99	n.m.
	0-2	n.m.	n.m.	n.m.	n.m.	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	4.77	0.087	5.44	30.0	1.30	n.m.	0.817	213	262
	5	4.25	0.102	5.71	4.02	0.175	n.m.	0.116	10.3	17.1
	10	22.7	0.252	28.6	10.7	1.13	n.m.	0.236	21.4	30.0
	30	2.20	0.078	3.06	2.86	0.202	n.m.	0.081	16.3	23.3
	50	1.02	0.065	1.27	5.04	0.186	n.m.	0.057	9.81	13.0
	80	1.03	0.068	1.81	7.66	0.088	n.m.	0.066	17.7	21.8
	200	0.68	0.079	2.03	5.88	0.662	n.m.	0.093	13.7	16.1
Station B	0	25.7	0.117	28.9	56.9	9.78	n.m.	1.22	187	218
	5	4.02	0.088	4.83	3.45	0.231	n.m.	0.134	12.5	21.6
	10	10.9	0.179	18.5	4.73	0.599	n.m.	0.143	12.9	21.9
	30	1.86	0.077	2.81	6.65	0.159	n.m.	0.077	5.10	8.05
	50	1.10	0.072	2.48	4.79	0.099	n.m.	0.074	9.37	14.3
	80	1.17	0.074	1.69	7.89	0.232	n.m.	0.171	25.7	32.0
Woodfibre	0-1	1.75	0.012	1.85	33.6	1.05	n.m.	0.903	303	439
	0-2	1.57	0.011	1.62	37.4	1.01	n.m.	0.962	282	378
	0-3	1.46	0.010	2.64	43.0	0.974	n.m.	0.924	283	368
Porteau	0-1	4.97	0.037	4.02	20.6	2.18	n.m.	1.02	274	345
	0-2	5.52	0.035	4.53	27.3	1.99	n.m.	0.979	243	327

HS 0794 Profiles

Date	27/7/94
Time	08:00 - 10:30

Wind [km/h]	0.00
River discharge [m3/s]	467
Creek discharge [m3/s]	0.75

Tides
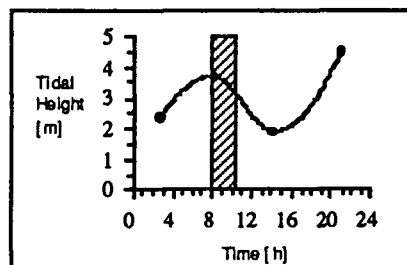
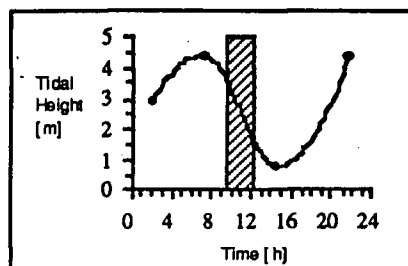|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	14.6	3.68	7.63	6.76	0.041
	5	13.0	23.3	7.85	4.81	0.125
	10	11.4	27.3	7.60	4.04	0.034
	30	9.48	24.5	7.62	6.42	n.m.
	50	9.07	29.9	7.58	6.00	n.m.
	80	8.43	30.4	7.59	6.59	n.m.
	200	9.22	30.9	7.40	1.57	n.m.
Station B	0	17.2	2.57	7.59	6.85	0.059
	5	13.8	23.7	7.98	5.57	0.211
	10	11.2	26.9	7.61	4.30	0.024
	30	9.59	29.5	7.59	4.13	n.m.
	50	9.26	29.8	7.52	5.66	n.m.
	80	8.43	30.5	7.21	6.51	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	2.48	0.027	17.0	53.4	1.25	n.m.	0.790	278	497
	5	2.72	0.079	10.4	8.44	0.176	n.m.	0.166	28.1	56.1
	10	13.2	0.162	24.8	5.50	0.604	n.m.	0.147	18.6	35.7
	30	7.12	0.116	17.2	4.22	0.692	n.m.	0.298	46.4	89.8
	50	2.16	0.069	6.43	6.54	{0.073}	n.m.	{0.699}	{13.9}	{21.4}
	80	5.34	0.102	13.1	6.12	0.557	n.m.	0.235	50.9	100
	200	0.91	0.068	4.07	6.65	0.133	n.m.	0.109	32.9	58.5
Station B	0	7.68	0.096	19.2	17.3	5.26	n.m.	1.37	295	545
	5	2.73	0.066	4.97	3.55	0.147	n.m.	0.152	13.5	24.3
	10	9.91	0.155	19.5	2.93	{0.455}	n.m.	{0.214}	{13.2}	{25.7}
	30	2.04	0.073	4.99	7.94	0.132	n.m.	0.093	12.1	17.3
	50	7.47	0.123	15.1	2.55	0.717	n.m.	0.222	31.8	58.8
	80	7.94	0.123	13.2	2.67	0.547	n.m.	0.163	25.9	46.7

HS 0894 Profiles

Date   26/8/94
Time   07:30 - 09:30

Wind [km/h]   0.04
River discharge [m3/s]   270
Creek discharge [m3/s]   0.44

Tides

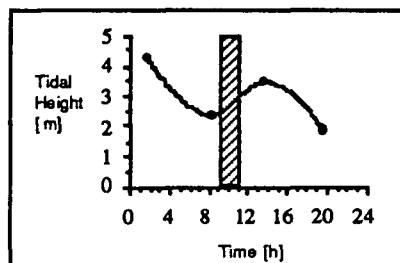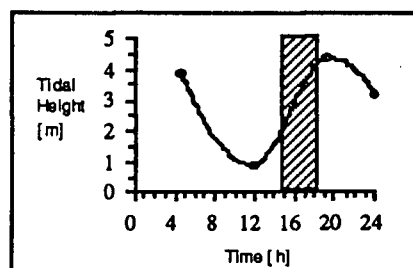|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]	DOC [mg C/L]
Station A	0	14.7	15.2	8.11	6.93	0.787	n.m.
	5	12.1	27.5	7.64	4.98	0.588	n.m.
	10	10.6	28.7	7.46	4.38	0.059	n.m.
	30	9.20	30.1	7.64	3.70	n.m.	n.m.
	50	8.83	30.5	7.62	3.53	n.m.	n.m.
	80	8.51	30.8	7.53	3.27	n.m.	n.m.
	200	9.19	31.4	7.36	1.83	n.m.	n.m.
Station B	0	15.6	15.2	8.18	7.95	0.583	n.m.
	5	12.1	27.6	7.86	8.64	0.802	n.m.
	10	10.6	28.6	7.61	4.64	0.284	n.m.
	30	9.13	30.1	7.66	3.36	n.m.	n.m.
	50	9.07	30.3	7.75	3.53	n.m.	n.m.
	80	8.59	30.6	7.76	3.44	n.m.	n.m.
Outfall	0	17.2	14.9	8.18	6.85	0.968	5.026
	5	12.9	27.1	7.91	5.32	1.44	2.019
	10	9.11	29.1	7.59	4.04	0.0813	3.307
	15	8.44	29.9	7.64	4.04	0.0454	2.778
	20	8.17	29.9	7.73	4.04	0.025	1.354
	25	8.03	29.9	7.70	4.13	0.031	2.241

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	1.94	0.060	4.25	11.7	0.193	n.m.	0.228	32.0	47.2
	5	6.07	0.117	9.91	3.79	0.339	n.m.	0.183	16.3	16.9
	10	7.02	0.119	11.7	6.69	{0.647}	n.m.	{0.167}	{22.2}	{22.98}
	30	1.48	0.066	1.40	5.08	0.199	n.m.	0.108	18.2	12.1
	50	1.06	0.065	1.18	4.60	0.193	n.m.	0.081	18.9	15.5
	80	1.09	0.066	2.38	4.61	0.216	n.m.	0.113	20.4	14.6
	200	0.789	0.066	1.42	4.03	0.103	n.m.	0.110	28.7	31.9
Station B	0	2.96	0.051	2.71	26.6	0.261	n.m.	0.374	114	157
	5	4.89	0.107	7.39	1.50	0.215	n.m.	0.088	20.0	13.7
	10	10.9	0.159	14.7	4.05	0.566	n.m.	0.113	17.1	18.0
	30	1.80	0.068	1.40	5.85	0.145	n.m.	0.102	17.2	20.6
	50	0.601	0.065	0.958	{0.083}	0.181	n.m.	0.071	18.8	24.4
	80	0.979	0.065	0.805	7.26	0.222	n.m.	0.179	32.0	43.8
Outfall	0	3.81	0.059	4.14	12.8	0.984	n.m.	0.711	129	207
	5	8.34	0.117	9.42	2.13	0.402	n.m.	0.150	7.06	12.9
	10	54.0	0.481	67.8	4.27	10.3	n.m.	2.609	25.1	82.3
	15	91.5	0.779	127	2.76	29.5	n.m.	5.804	40.6	141
	20	2.35	0.066	3.24	3.50	0.333	n.m.	0.136	25.6	27.9
	25	1.67	0.072	2.15	5.85	0.362	n.m.	2.022	35.0	32.2

HS 0994 Profiles

Date	26/9/94
Time	08:00 - 10:00

Wind [km/h]	0.00
River discharge [m3/s]	254
Creek discharge [m3/s]	0.3

Tides

	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	13.2	9.93	7.64	8.87	1.76
	5	12.9	25.8	7.68	7.21	1.06
	10	11.3	28.8	7.42	5.44	0.535
	30	9.24	30.0	7.39	5.31	0.017
	50	8.80	30.5	7.32	5.16	0.015
	80	9.11	30.9	7.27	4.99	0.011
	200	9.17	31.2	7.00	2.75	0.005
Station B	0	13.0	8.73	7.23	9.37	18.1
	5	13.1	26.0	7.48	7.55	0.986
	10	11.3	28.7	7.21	5.39	0.467
	30	9.21	29.9	7.31	5.23	n.m.
	50	9.08	30.3	7.25	5.14	n.m.
	80	9.15	30.7	7.16	4.63	n.m.
off Porteau	0	15.3	12.6	7.85	9.28	1.64
	5	12.9	27.3	7.59	8.23	1.93
	10	11.1	28.7	7.40	5.82	0.541
	30	9.38	30.0	7.40	5.10	n.m.
	50	9.08	30.3	7.33	5.10	n.m.
	80	9.55	30.7	7.31	4.45	n.m.
	140	9.05	31.0	7.11	3.17	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	1.42	0.039	1.53	4.39	0.557	n.m.	0.967	267	397
	5	1.65	0.074	1.66	3.73	0.100	n.m.	0.125	19.3	33.0
	10	2.54	0.077	1.71	1.85	0.108	n.m.	0.099	11.3	19.2
	30	1.89	0.066	1.58	2.04	0.122	n.m.	0.091	14.0	21.8
	50	1.04	0.061	1.42	1.17	0.062	n.m.	0.072	9.74	14.4
	80	0.682	0.062	0.827	1.18	0.071	n.m.	0.099	17.4	29.6
	200	0.725	0.060	2.14	0.801	0.064	n.m.	0.086	10.4	16.9
Station B	0	1.28	0.041	1.71	10.2	0.754	n.m.	1.00	220	322
	5	0.765	0.056	0.978	2.53	0.121	n.m.	0.178	17.8	31.8
	10	2.49	0.072	2.82	2.38	0.172	n.m.	0.106	8.97	15.5
	30	1.59	0.062	1.47	2.37	0.152	n.m.	0.098	11.3	14.8
	50	0.837	0.064	1.39	2.48	0.128	n.m.	0.110	19.8	28.9
	80	0.548	0.062	0.702	2.75	0.114	n.m.	0.116	21.0	30.8
off Porteau	0	1.19	0.039	2.40	26.4	0.116	n.m.	0.223	36.8	50.4
	5	1.41	0.065	1.99	1.74	0.060	n.m.	0.091	11.8	18.7
	10	0.892	0.071	2.72	1.29	0.057	n.m.	0.149	8.05	12.4
	30	0.791	0.069	1.15	1.16	0.044	n.m.	0.048	4.61	7.07
	50	0.854	0.068	1.13	2.06	0.120	n.m.	0.264	3.29	5.72
	80	0.521	0.071	0.699	2.93	0.062	n.m.	0.125	8.5	10.2
	140	0.962	0.066	1.57	4.74	0.336	n.m.	0.608	177	271

HS 1094 Profiles

Date	2/11/94
Time	09:00 - 11:00 (?)
Wind [km/h]	3.90
River discharge [m3/s]	102
Creek discharge [m3/s]	1.35

Tides
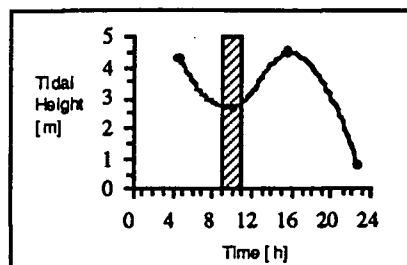
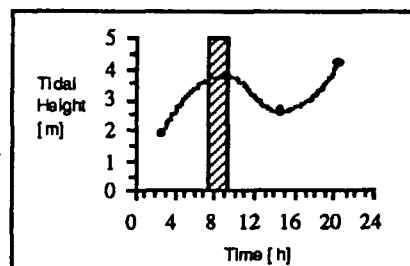|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	8.75	21.1	7.60	6.44	2.93
	5	9.72	24.3	7.67	5.85	3.89
	10	10.4	26.1	7.65	5.62	2.71
	30	9.02	30.8	7.29	3.50	n.m.
	50	9.20	31.1	7.30	3.28	n.m.
	80	9.27	31.3	7.00	2.99	n.m.
	200	9.16	31.4	6.64	1.72	n.m.
Station B	0	8.83	21.8	7.74	6.23	3.31
	5	9.85	23.9	7.76	6.12	1.99
	10	10.1	24.7	7.75	5.51	2.55
	30	9.05	30.6	7.44	3.51	n.m.
	50	9.29	30.9	7.47	3.24	n.m.
	80	9.03	31.0	7.34	3.07	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	0.685	0.057	6.32	6.41	0.184	n.m.	0.179	37.2	34.8
	5	2.78	0.062	3.74	12.3	0.151	n.m.	0.182	19.7	23.1
	10	1.83	0.064	3.33	6.41	0.065	n.m.	0.090	9.72	11.7
	30	1.03	0.067	2.80	11.1	0.077	n.m.	0.126	18.8	24.3
	50	1.94	0.064	4.01	7.07	0.074	n.m.	0.106	19.1	27.3
	80	0.862	0.067	6.63	6.76	0.070	n.m.	0.370	12.2	17.6
	200	0.614	0.065	3.89	4.11	0.102	n.m.	0.223	20.8	32.3
Station B	0	2.75	0.067	4.86	6.09	0.435	n.m.	0.247	39.5	38.9
	5	1.21	0.058	2.46	14.3	0.144	n.m.	0.128	31.5	31.0
	10	2.74	0.064	3.90	8.28	0.108	n.m.	0.086	17.8	12.4
	30	1.03	0.066	2.98	2.67	0.175	n.m.	0.144	28.0	26.4
	50	0.689	0.065	1.86	6.09	0.087	n.m.	0.098	17.9	17.9
	80	0.685	0.064	1.14	9.39	0.153	n.m.	0.197	25.6	30.7

HS 0195 Profiles

Date   16/1/95
Time   10:00 - 13:00

Wind [km/h]   1.08
River discharge [m3/s]   69.5
Creek discharge [m3/s]   1.84

Tides

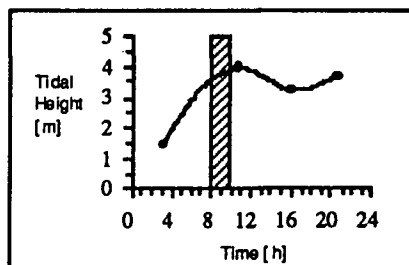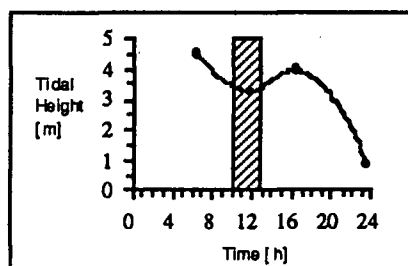|	Depth [m]	Temp. [°C]	Salinity [per mil]	pH	O2 [mL/L]	chl. a [µg/L]
Station A	0	6.35	25.5	n.m.	6.75	0.138
	5	7.53	28.7	n.m.	5.91	0.112
	10	7.75	29.1	n.m.	5.71	0.077
	30	8.31	30.1	n.m.	5.20	n.m.
	50	8.44	30.2	n.m.	5.05	n.m.
	80	9.42	30.8	n.m.	3.17	n.m.
	200	9.18	30.9	n.m.	1.60	n.m.
Station B	0	6.55	25.3	n.m.	6.63	0.083
	5	7.55	28.7	n.m.	5.86	0.084
	10	7.71	29.0	n.m.	5.72	0.093
	30-1	8.32	30.1	n.m.	5.25	n.m.
	30-2	8.31	30.1	n.m.	5.21	n.m.
	30-3	8.32	30.1	n.m.	5.37	n.m.
	50	8.45	30.2	n.m.	5.09	n.m.
	80	9.39	30.8	n.m.	3.17	n.m.

	Depth [m]	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
Station A	0	10.8	0.115	9.93	3.66	0.333	n.m.	0.386	29.2	23.6
	5	1.80	0.071	2.08	3.61	0.133	n.m.	0.107	13.3	15.1
	10	3.82	0.081	3.19	1.85	n.m.	n.m.	n.m.	n.m.	n.m.
	30	0.730	0.069	1.04	1.87	0.093	n.m.	0.127	13.8	19.9
	50	0.492	0.070	0.944	3.33	0.073	n.m.	0.182	14.2	18.9
	80	0.694	0.070	0.743	5.37	0.103	n.m.	0.094	18.0	23.5
	200	0.704	0.063	1.02	3.90	0.102	n.m.	0.119	19.6	32.8
Station B	0	14.7	0.133	12.8	4.82	3.32	n.m.	0.487	40.0	32.0
	5	9.61	0.108	7.97	3.07	0.779	n.m.	0.161	18.8	19.2
	10	2.94	0.077	2.29	2.43	0.233	n.m.	0.083	14.1	15.8
	30-1	0.838	0.070	1.12	2.66	0.140	n.m.	0.129	15.9	24.3
	30-2	0.659	0.069	0.759	1.36	0.106	n.m.	0.094	15.1	23.6
	30-3	0.660	0.069	0.744	2.36	0.100	n.m.	0.096	14.9	24.2
	50	1.76	0.087	1.09	2.13	n.m.	n.m.	n.m.	n.m.	n.m.
	80	0.686	0.067	0.720	2.41	0.071	n.m.	0.138	23.8	33.7

A.2.3. Mixing Experiments

MIX1
filtered Britannia Creek and filtered Howe Sound water

Date   11/1/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
MIX 1.9	30	0.00	6.40	6.6	0.873	< 0.002	1.375	0.072	3.147
MIX 1.1	30	2.45	n.m.	13.4	1.13	< 0.002	1.25	0.092	2.61
MIX 1.5	30	2.45	n.m.	n.m.	1.46	< 0.002	1.99	0.126	2.61
MIX 1.2	30	4.73	n.m.	17.0	1.95	< 0.002	1.15	0.103	1.98
MIX 1.6	30	4.91	n.m.	n.m.	1.82	< 0.002	1.16	0.223	1.91
KIN 1.4	30	12.3	n.m.	27.8	1.41	< 0.002	0.894	0.086	1.35
KIN 1.5	30	12.3	n.m.	28.3	1.14	< 0.002	0.746	0.107	1.88
MIX 1.4	30	18.4	n.m.	44.1	0.560	< 0.002	0.258	0.109	1.12
MIX 1.7	30	18.4	n.m.	38.4	0.546	< 0.002	0.330	0.064	0.921
MIX 1.8	30	24.6	7.83	65.5	0.069	< 0.002	0.281	0.023	0.738

MIX2
repeat of MIX1 using water stored for 1 week

Date   18/1/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
MIX 2.9	30	0.00	n.m.	n.m.	1.54	< 0.002	2.32	0.073	n.m.
MIX 2.7	30	2.46	n.m.	n.m.	1.93	< 0.002	1.27	0.071	n.m.
MIX 2.8	30	2.46	n.m.	n.m.	1.72	< 0.002	1.48	0.097	n.m.
MIX 2.5	20	4.91	n.m.	n.m.	2.36	< 0.002	1.40	0.084	n.m.
MIX 2.6	30	4.91	n.m.	n.m.	2.31	< 0.002	1.66	0.144	n.m.
MIX 2.1	30	12.3	n.m.	n.m.	1.80	< 0.002	0.771	0.077	n.m.
MIX 2.2	30	12.3	n.m.	n.m.	2.16	< 0.002	1.46	0.154	n.m.
MIX 2.3	6	18.4	n.m.	n.m.	0.640	< 0.002	0.071	0.059	n.m.
MIX 2.10	30	24.6	n.m.	n.m.	0.088	< 0.002	0.161	0.017	n.m.

KIN1
as MIX1, but variable reaction times

Date   11/1/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
KIN 1.3	5	12.3	n.m.	n.m.	1.27	< 0.002	1.32	0.063	n.m.
KIN 1.4	10	12.3	n.m.	n.m.	1.42	< 0.002	1.01	0.088	n.m.
KIN 1.5	20	12.3	n.m.	n.m.	1.05	< 0.002	0.66	0.095	n.m.
KIN 1.6	30	12.3	n.m.	n.m.	1.40	< 0.002	0.69	0.089	n.m.
MIX 1.3	30	12.3	n.m.	n.m.	1.36	< 0.002	0.81	0.069	n.m.
KIN 1.2	1260	12.3	n.m.	n.m.	7.92	< 0.002	2.95	0.286	n.m.

KIN2
repeat of KIN1 with stored water

Date   18/1/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
KIN 2.5	1	12.3	n.m.	n.m.	1.68	< 0.002	0.257	0.089	n.m.
KIN 2.3	10	12.3	n.m.	n.m.	1.63	< 0.002	1.41	0.095	n.m.
KIN 2.4	20	12.3	n.m.	n.m.	1.77	< 0.002	1.27	0.106	n.m.
MIX 2.2	34	12.3	n.m.	n.m.	2.16	< 0.002	1.46	0.154	n.m.
MIX 2.1	30	12.3	n.m.	n.m.	1.80	< 0.002	0.771	0.077	n.m.
KIN 2.2	60	12.3	n.m.	n.m.	3.18	< 0.002	2.17	0.152	n.m.
KIN 2.1	1420	12.3	n.m.	n.m.	11.9	< 0.002	2.75	0.398	n.m.

MIX3
as MIX1, but with different filter pore sizes

Date   18/1/96

Label	time [min.]	Salinity [per mil]	Filter pore size [µm]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]
MIX 3.12	0	0.00	0.1	n.m.	n.m.	7.33	< 0.002	8.17	0.260
MIX 3.11	0	0.00	0.4	n.m.	n.m.	2.34	< 0.002	5.67	0.137
MIX 3.2	30	2.46	0.1	n.m.	n.m.	20.9	< 0.002	12.1	0.594
MIX 3.6	180	2.46	0.4	n.m.	n.m.	2.14	< 0.002	4.93	0.093
MIX 3.3	30	4.91	0.1	n.m.	n.m.	25.4	< 0.002	14.5	0.690
MIX 3.7	180	4.91	0.4	n.m.	n.m.	1.67	< 0.002	4.57	0.110
MIX 3.8	30	12.3	0.1	n.m.	n.m.	12.9	< 0.002	12.2	1.36
MIX 3.9	30	12.3	0.4	n.m.	n.m.	1.583	< 0.002	6.9	0.23
MIX 3.13	30	12.3	0.4	n.m.	n.m.	1.64	< 0.002	5.96	0.193
MIX 3.4	180	12.3	0.4	n.m.	n.m.	1.20	< 0.002	6.50	0.125
MIX 3.1	180	12.3	0.4	n.m.	n.m.	2.67	< 0.002	5.82	0.452
MIX 3.10	30	18.4	0.1	n.m.	n.m.	4.61	< 0.002	13.1	1.33
MIX 3.5	180	18.4	0.4	n.m.	n.m.	0.346	< 0.002	6.87	0.183
MIX 3.14	0	24.6	0.4	n.m.	n.m.	0.071	< 0.002	0.651	0.032

MIX4
as MIX1, but with new batch of Britannia Creek and Howe Sound water, both end-members unfiltered

Date   5/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
MIX 4.11	30	0.00	6.53	0.647	13.2	0.0022	0.421	571	273
MIX 4.12	30	0.00	6.53	n.m.	13.7	0.0023	0.451	587	276
MIX 4.2	30	0.44	6.68	0.694	25.0	0.0022	0.550	569	451
MIX 4.31	30	0.87	6.74	0.727	66.6	0.0036	1.53	603	674
MIX 4.32	30	0.88	6.85	0.749	69.0	0.0024	1.47	611	745
MIX 4.4	30	1.75	7.01	0.831	194	0.0038	4.37	649	759
MIX 4.5	30	2.62	7.17	0.788	260	0.0049	7.35	618	766
MIX 4.61	30	3.94	7.32	0.744	302	0.0049	9.29	593	699
MIX 4.62	30	3.94	7.35	0.73	278	0.0047	8.96	549	614
MIX 4.7	30	6.56	7.61	0.421	172	0.0038	9.39	501	578
MIX 4.81	30	8.75	7.91	0.232	1.12	0.0014	1.57	434	688
MIX 4.82	30	8.75	7.91	n.m.	1.03	0.0012	1.41	446	643

MIX4 (continued)

Label	Cu diss. [µg/L]	Cd diss. [µg/L]	Zn diss. [µg/L]	Fe diss. [µg/L]	Al diss. [µg/L]
MIX 4.11	1530	3.05	560	93.2	n.m.
MIX 4.12	913	3.09	329	107	n.m.
MIX 4.2	1430	2.98	521	91.2	n.m.
MIX 4.31	1280	2.77	488	73.2	n.m.
MIX 4.32	1220	2.74	481	73.2	n.m.
MIX 4.4	971	2.30	434	8.50	n.m.
MIX 4.5	727	2.07	372	3.70	n.m.
MIX 4.61	484	1.54	287	5.60	n.m.
MIX 4.62	494	1.58	300	39.1	n.m.
MIX 4.7	159	0.650	142	5.20	n.m.
MIX 4.81	2.70	0.040	2.90	6.26	n.m.
MIX 4.82	2.70	0.022	16.3	7.60	n.m.

MIX5

as MIX4, but with filtered Britannia Creek water and unfiltered Howe Sound water

Date   5/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
MIX 5.1=7.1	30	0.00	n.m.	0.178	0.627	0.0005	0.540	21.9	7.67
MIX 5.2	30	0.44	n.m.	n.m.	6.10	0.0005	0.175	42.8	168
MIX 5.31	30	0.87	n.m.	n.m.	33.8	0.0009	0.662	67.9	399
MIX 5.32	30	0.88	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
MIX 5.4	30	1.75	n.m.	n.m.	118	0.0017	2.76	133	288
MIX 5.5	30	2.63	n.m.	n.m.	191	0.0026	4.97	198	514
MIX 5.61	30	3.94	n.m.	n.m.	216	0.0031	6.65	282	558
MIX 5.62	30	3.94	n.m.	n.m.	213	0.0027	6.26	259	213
MIX 5.7	30	6.96	n.m.	n.m.	116.82	0.0024	6.05	371	433
MIX 5.8=4.81	30	8.75	7.91	0.232	1.12	0.0014	1.57	434	688

MIX6

as MIX4, but with unfiltered Britannia Creek water and filtered Howe Sound water

Date   5/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
MIX 6.1=4.11	30	0.00	6.53	0.647	13.2	0.0022	0.421	571	273
MIX 6.2	30	0.44	n.m.	n.m.	20.7	0.0012	0.313	569	454
MIX 6.31	30	0.87	n.m.	n.m.	62.3	0.0018	1.04	583	743
MIX 6.32	30	0.88	n.m.	n.m.	65.1	0.0019	1.01	547	584
MIX 6.4	30	1.75	n.m.	n.m.	200	0.0033	4.21	542	512
MIX 6.5	30	2.62	n.m.	n.m.	254	0.0036	6.40	464	402
MIX 6.61	30	3.93	n.m.	n.m.	268	0.0038	8.16	392	351
MIX 6.62	30	3.94	n.m.	n.m.	252	0.0036	7.10	374	275
MIX 6.7	30	6.59	n.m.	n.m.	141	0.0021	6.49	189	146
MIX 6.8=9.8	30	8.75	7.91	0.342	0.063	<0.001	0.076	4.03	8.16

MIX7
as MIX4, but with filtered Britannia Creek and filtered Howe Sound water

Date   5/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
MIX 7.1	30	0.00	n.m.	0.178	0.627	0.0005	0.540	21.9	7.67
MIX 7.2	30	0.44	n.m.	0.272	4.86	0.0006	0.145	27.4	224
MIX 7.31	30	0.87	n.m.	0.266	24.9	0.0006	0.467	29.3	405
MIX 7.32	30	0.87	n.m.	0.361	24.7	0.0007	0.478	27.5	406
MIX 7.4	30	1.75	n.m.	0.376	103	0.0014	2.52	69.8	408
MIX 7.5	30	2.63	n.m.	0.450	157	0.0017	3.89	78.0	427
MIX 7.61	30	3.94	n.m.	0.433	167	0.0016	4.27	56.0	149
MIX 7.62	30	3.94	n.m.	0.493	170.24	0.0019	4.411	66.4	295.3
MIX 7.7	30	6.56	n.m.	0.223	7.05	0.0002	0.239	9.76	6.72
MIX 7.8=9.8	30	8.75	7.91	0.342	0.063	<0.001	0.076	4.03	8.16

MIX8
1:1 mixture of filtered 4100 drainage and sewage, mixed with filtered Howe Sound water

Date   8/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
MIX 8.01	30	0.02	n.m.	n.m.	74.9	0.0427	142	n.m.	95.6
MIX 8.02	30	0.02	n.m.	n.m.	2.44	0.0017	0.098	11.6	7.36
MIX 8.03	30	0.02	6.93	7.36	1715	0.5302	277	106	2430
MIX 8.1	30	0.46	6.99	6.96	1536	0.4281	295	91.6	2413
MIX 8.2	30	0.88	6.61	6.86	2057	0.4537	374	148	3867
MIX 8.22	30	0.46	n.m.	n.m.	3125	0.8669	596	182	4429
MIX 8.3	30	1.77	6.84	6.64	1895	0.3094	312	107	2519
MIX 8.4	30	2.64	7.01	6.28	1811	0.2953	317	75.8	756
MIX 8.5	30	3.95	6.94	5.05	1367	0.1691	245	98.2	389
MIX 8.52	30	3.95	7.17	5.52	1518	0.1947	290	136	2079
MIX 8.6	30	6.57	7.31	2.80	120	0.0918	33.3	5.20	109
MIX 9.8	30	8.75	7.91	0.34	0.063	0.0015	0.076	4.03	8.16

Label	Cu diss. [μg/L]	Cd diss. [μg/L]	Zn diss. [μg/L]	Fe diss. [μg/L]	Al diss. [μg/L]
MIX 8.01	9811	81	18600	46.2	12100
MIX 8.02	110	1.15	25.8	182	143
MIX 8.03	2570	44.0	6530	62	1700

MIX9
as MIX8, but without sewage

Date   8/6/96

Label	time [min.]	Salinity [per mil]	pH	TPC [mg C/L]	Cu part. [µg/L]	Cd part. [µg/L]	Zn part. [µg/L]	Fe part. [µg/L]	Al part. [µg/L]
MIX 9.1	30	0.02	4.43	n.m.	1.56	0.0098	2.34	1.07	2.52
MIX 9.2	30	0.46	4.52	0.031	1.17	0.0073	1.67	1.49	47.4
MIX 9.31	30	0.89	4.57	0.117	2.53	0.0119	2.98	2.88	37.0
MIX 9.32	30	0.89	4.57	0.056	2.33	0.0140	3.37	1.70	4.67
MIX 9.4	30	1.76	4.66	0.294	3.36	0.0116	2.93	12.71	439.35
MIX 9.5	30	2.64	4.72	0.398	16.4	0.0084	2.78	16.8	751
MIX 9.61	30	3.95	4.88	0.714	43.4	0.0046	3.62	16.7	1784
MIX 9.62	30	3.94	4.94	0.560	44.5	0.0076	4.10	13.3	1160
MIX 9.7	30	6.58	6.80	1.15	493	0.0117	47.8	15.1	2331
MIX 9.8	30	8.75	7.91	0.342	0.063	<0.001	0.076	4.03	8.16

For experiments MIX4 through MIX9, samples labelled MIX_.8 are seawater, MIX_.1 are fresh water.
Samples MIX9.1 and 8.01 are 4100 drainage, 8.02 is sewage, and 8.03 is a 1:1 mixture of filtered AMD and sewage.

A.2.4. Sediment Traps

Station	weight [g]	Cu [ppm]	Zn [ppm]	Al2O3 [%]	Fe2O3 [%]
A 30	3.31	128	121	15.7	5.44
A 30 F	3.11	181	143	16.0	5.73
A 50	3.80	115	121	16.5	5.37
A 50 F	3.76	108	134	16.0	5.55
A 200	7.27	104	128	17.3	6.00
A 200 F	7.12	104	118	15.9	5.75
B 30	3.54	411	99.0	15.0	5.86
B 30 F	3.39	378	117	16.1	5.86
B 50	4.16	356	115	14.9	5.92
B 50 F	4.20	482	150	16.3	6.02
B 80	5.52	360	136	15.3	6.21
B 80 F	5.42	315	137	16.5	6.40

Samples with postscript "F" contained formaldehyde as a preservative

A.2.5. Britannia Creek February 1996

Date   12/2/96
Time   14:00 - 18:00

Station Description	Station #	pH	PON [mg N/L]	POC [mg C/L]	DOC [mg C/L]	SO4 diss. [μM]
Britannia Creek before 2200	1	6.98	0.0092	0.073	1.41	41
2200 Portal	2	3.11	0.0101	0.049	1.04	15500
Jane Creek before 2200	3	7.05	0.0144	0.279	0.39	543
Jane Creek after 2200	4	3.60	0.0108	0.126	1.29	3620
Britannia Creek 150 m after 220(	5	4.82	0.0107	0.472	0.29	789
Britannia Creek 800 m after 220(	6	5.99	0.0100	0.432	0.53	314
Britannia Creek at mouth	7	6.40	0.0106	0.347	0.65	272
Furry Creek	8	7.09	0.0047	0.052	n.m.	94

| Station #	Cu diss. [μg/L]	Cd diss. [μg/L]	Zn diss. [μg/L]	Fe diss. [μg/L]	Al diss. [μg/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
1	<1	<0.1	0.731	9.90	36.6	0.120	<0.002	0.111	50.3	81.2
2	52000	211	31800	30200	44700	23.3	0.094	50.8	992	44.9
3	165	2.69	509	<1	36.7	76	0.0148	8.16	40.6	663
4	14000	53.5	9000	4040	11800	9.76	0.0217	2.83	3670	50.3
5	1230	5.63	822	68.4	771	34.9	0.0051	0.655	525	562
6	805	4.00	603	85.2	169	17.1	0.0048	1.08	424	692
7	454	2.52	410	25.4	32.3	40.5	0.0061	1.49	176	463
8	6.11	<0.1	2.69	7.00	52.6	0.160	<0.002	0.075	14.4	30.4

A.2.6. Bioassay

Culture	Day of exp.	TPC [mg C/L]	TPN [mgN/L]	NO3 [μM]	SiO2 [μM]	NH3 [μM]	PO4 [μM]	log cell density [cells/L]	chl. a [mg/L]	Fluoresc. [arbitrary units]
Control 1	1	n.m.	n.m.	66.5	52.7	1.54	3.43	7.02	27.7	2.50
Control 1	4	6.29	0.80	0.10	0.01	0.02	0.16	7.84	236	14.5
Control 2	4	6.67	0.77	0.07	0.31	0.00	0.08	7.71	225	14.6
Control 3	4	7.09	0.83	0.16	0.67	0.04	0.08	7.83	192	13.6
Control 1	14	15.9	0.65	0.23	10.2	0.17	0.10	7.85	136	9.85
Low 1	1	n.m.	n.m.	66.5	52.7	1.54	3.43	7.02	27.7	2.50
Low 1	4	3.88	0.38	1.00	0.89	0.14	0.09	8.1	145	10.5
Low 2	4	4.59	0.49	0.30	0.09	0.12	0.09	n.m.	127	10.2
Low 3	4	7.69	0.81	0.50	0.90	0.21	0.09	n.m.	150	10.2
Low 1	14	12.8	0.59	0.55	11.5	0.19	0.12	8.13	70.4	9.79
Medium 1	1	n.m.	n.m.	66.5	52.7	1.54	3.43	7.02	27.7	2.50
Medium 1	4	4.74	0.55	0.46	0.89	0.17	0.06	8.38	62.1	5.00
Medium 2	4	4.79	0.64	0.17	11.7	0.15	0.06	n.m.	76.1	6.02
Medium 3	4	6.92	0.77	0.10	1.91	0.13	0.08	n.m.	72.5	5.88
Medium 1	14	13.4	0.62	0.30	1.55	0.15	0.09	8.06	38.0	7.05
High 1	1	n.m.	n.m.	66.5	52.7	1.54	3.43	7.02	27.7	2.50
High 1	4	0.70	0.14	62.8	42.7	0.13	2.29	6.66	11.9	0.01
High 2	4	1.08	0.24	68.0	66.9	0.34	2.49	n.m.	13.1	0.05
High 3	4	0.87	0.20	65.0	42.5	0.21	2.35	n.m.	3.8	0.25
High 1	14	6.29	0.43	0.28	2.28	0.15	0.02	8.37	67.3	8.14

Culture	Day of exp.	Cu diss. [μg/L]	Cd diss. [μg/L]	Zn diss. [μg/L]	Fe diss. [μg/L]	Cu part. [μg/L]	Cd part. [μg/L]	Zn part. [μg/L]	Fe part. [μg/L]	Al part. [μg/L]
Control 1	1	5.59	0.071	4.37	3.47	1.06	0.0020	1.33	47.8	86.0
Control 1	4	3.47	0.046	1.91	2.11	1.29	0.0248	2.68	25.6	68.2
Control 2	4	3.02	0.050	0.472	1.94	n.m.	n.m.	n.m.	n.m.	n.m.
Control 3	4	3.37	0.059	0.965	2.80	1.20	0.0206	2.67	24.5	55.6
Control 1	14	3.79	0.079	7.96	1.14	1.15	0.0112	2.29	40.4	67.6
Low 1	1	6.38	0.087	5.56	2.67	1.98	0.0020	2.01	47.7	97.6
Low 1	4	5.56	0.078	0.442	1.36	2.63	0.0143	7.56	39.4	80.9
Low 2	4	5.20	0.079	0.398	1.54	2.59	0.0149	7.61	36.0	80.3
Low 3	4	8.55	0.080	1.69	3.43	2.42	0.0147	7.36	38.6	73.0
Low 1	14	5.67	0.091	1.70	0.900	2.21	0.0057	5.67	43.3	74.9
Medium 1	1	15.0	0.160	18.9	3.93	4.42	0.0020	3.38	55.8	68.0
Medium 1	4	12.9	0.154	1.09	2.71	6.05	0.0057	21.3	36.2	71.6
Medium 2	4	13.4	0.147	0.942	2.73	6.21	0.0078	23.9	38.8	73.9
Medium 3	4	13.7	0.156	1.42	2.67	5.90	0.0069	20.7	38.9	92.6
Medium 1	14	16.5	0.161	35.5	33.4	3.57	0.0020	9.06	22.0	49.3
High 1	1	54.7	0.521	89.3	2.50	32.7	0.0020	12.4	75.7	77.6
High 1	4	51.7	0.484	105	10.5	16.0	0.0020	7.07	36.2	65.8
High 2	4	58.5	0.527	97.7	6.10	20.1	0.0020	8.99	57.9	82.8
High 3	4	51.3	0.508	89.4	5.03	21.8	0.0020	9.38	65.8	90.0
High 1	14	44.4	0.520	51.4	1.55	21.5	0.0036	38.4	40.2	22.1

A.3. Box Model

A.3.1. Schematic and Conservation Equations
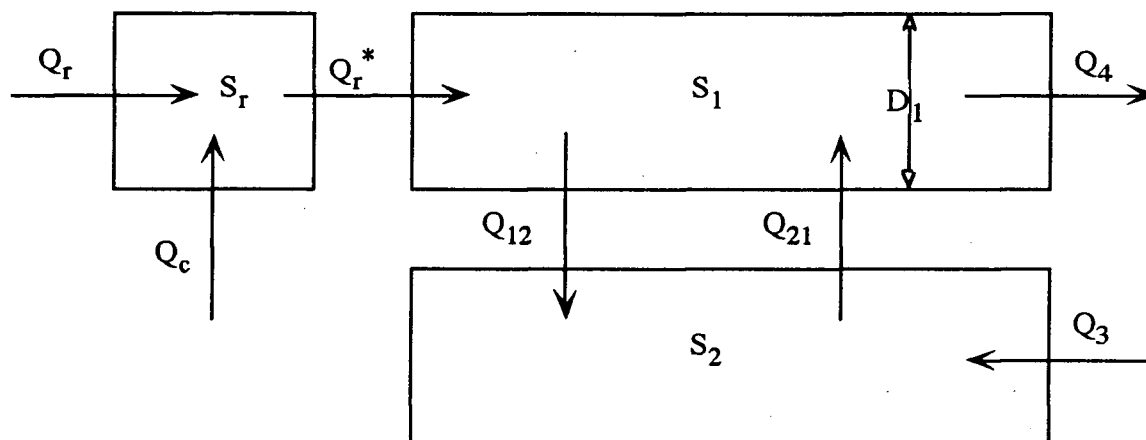
Equations:

Conservation of Volume: Upper Box: $Q_r^* + Q_{21} = Q_4 + Q_{12}$

Lower Box: $Q_{21} = Q_{12} + Q_3$

Conservation of Salt: Upper Box: $S_r Q_r^* + S_2 Q_{21} = S_1 Q_4 + S_1 Q_{12}$

Lower Box: $S_2 Q_{21} = S_1 Q_{12} + S_3 Q_3$

where
Q = volume flux
S = salinity
r = river
c = creek
1 = upper box
2 = lower box
3 = deep inflow
4 = surface outflow

Solving for the four unknown volume fluxes yields:

$$Q_4 = Q_r^*(S_3 - S_r)/(S_3 - S_1)$$

$$Q_3 = Q_r^*(S_1 - S_r)/(S_3 - S_1)$$

$$Q_{21} = Q_3(S_1 - S_3)/(S_1 - S_2)$$

$$Q_{12} = Q_3(S_2 - S_3)/(S_1 - S_2)$$

The upper box (depth D_1) was defined to extend from the surface to the bottom of the pycnocline, as inferred from hydrographic data at Station A. The lower boundary of the deeper box was determined from salinity profiles as the depth at which salinity became uniform. Salinities in the two boxes (S_1 and S_2) were calculated as the weighted mean of the salinity values recorded between the respective boundaries. S_3 in September was obtained from a salinity profile at Porteau Cove. In May and January, no such data were available, and S_3 was estimated instead from the salinity below the lower box. The velocity of the surface outflow (V_4) was calculated from the surface volume flux Q_4, the depth of the surface box (D_1) and an assumed channel width of 3 km.

Metal concentrations in surface water were estimated according to:

$$\left(C_{c,eff}.Q_c + C_2(Q_{21} - Q_{12}) + C_r Q_r\right)/Q_4$$

where $C =$ concentration

               $C_{c,\ eff.} =$ effective metal concentration in creek, corrected for removal in the mixing zone via $C_{c,\ eff.} = C \times$ (% flocculated)/100

A term $C_{m,\ eff.}Q_m$ was added to the sum in the above equation when accounting for the metal input from the submerged outfall.

A.3.2. Model Calculations

A.3.2.1. Box Model for HS 0594

DATASET:

HS 0594 profile at Station A for salinity
HS 0594 transect for metals

INPUT:

Q_r [m^3/s] =	440			
S_r [‰] =	0			
S_1 [‰] =	19.4			
S_2 [‰] =	27.4			
S_3 [‰] =	29.3			
D_1 [m] =	10.6			
Q_c [m^3/s] =	4.82			
Q_m [m^3/s] =	0.27			

	Cu	Cd	Zn
C_c [μg/L] =	2580	4.4	877
% flocculated creek =	37	0.3	2.8
C_2 [μg/L] =	3.19	0.0768	2.41
C_r [μg/L] =	1.5	0.015	5
C_m [μg/L] =	23500	104	27500
% flocculated mine =	50	5	10

OUTPUT:

Q_3 [m^3/s] =	862
Q_4 [m^3/s] =	1302
Q_{12} [m^3/s] =	205
Q_{21} [m^3/s] =	1067

V_4 [cm/s] = 4.10

	Cu	Cd	Zn
concentration at end of box [μg/L] =	8.64	0.072	6.44
measured surface concentration at Station A [μg/L] =	18.6	0.106	28.40
concentration at end of box (AMD incl.) [μg/L] =	11.1	0.093	11.57

A.3.2.2. Box Model for HS 0994

DATASET:

HS 0994 profiles at Stations A and E for salinity
HS 0994 transect for metals

INPUT:

Q_r [m^3/s] =	247			
S_r [‰] =	0			
S_1 [‰] =	15.1			
S_2 [‰] =	25.2			
S_3 [‰] =	29.3			
D_1 [m] =	2.84			
Q_c [m^3/s] =	0.424			
Q_m [m^3/s] =	0.1			
		Cu	Cd	Zn
C_c [μg/L] =		311	1.42	246
% flocculated creek =		0	0	9
C_2 [μg/L] =		1.89	0.0655	1.58
C_r [μg/L] =		1.5	0.015	5
C_m [μg/L] =		12500	115	18400
% flocculated mine =		50	5	10

OUTPUT:

Q_3 [m^3/s] =	263
Q_4 [m^3/s] =	510
Q_{12} [m^3/s] =	107
Q_{21} [m^3/s] =	369
V_4 [cm/s] =	5.98

	Cu	Cd	Zn
concentration at end of box [μg/L] =	1.23	0.042	3.42
measured surface concentration at Station A [μg/L] =	1.48	0.058	4.88
concentration at end of box (AMD incl.) [μg/L] =	3.19	0.064	6.68

A.3.2.3. Box Model for HS 0195

DATASET:

HS 0195 profile at Station A for salinity
HS 0195 transect for metals

INPUT:

Q_r [m^3/s] =	57.2			
S_r =	0			
S_1 =	27.1			
S_2 =	29.5			
S_3 =	32.0			
D_1 [m] =	2.99			
Q_c [m^3/s]=	1.51			
Q_m estimated [m^3/s] =	0.15			
		Cu	Cd	Zn
C_c [μg/L] =		976	3.10	699
% flocculated creek =		33	0.24	3
C_2 [μg/L] =		0.73	0.069	1.04
C_r [μg/L] =		1.5	0.015	5
C_m [μg/L] =		242000	76.3	17800
% flocculated mine =		50	5	10

OUTPUT:

Q_3 [m^3/s] =	319
Q_4 [m^3/s] =	376
Q_{12} [m^3/s] =	339
Q_{21} [m^3/s] =	658
V_4 [cm/s]	4.19

	Cu	Cd	Zn
concentration at end of box [μg/L] =	3.47	0.073	4.36
measured surface concentration at Station A [μg/L] =	10.8	0.115	9.93
concentration at end of box (AMD incl.) [μg/L] =	8.29	0.102	10.8