

BEHAVIOUR OF SOME TRACE METALS  
IN SEDIMENTS OF THE  
FRASER RIVER DELTA-FRONT,  
SOUTHWESTERN BRITISH COLUMBIA

by

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## ABSTRACT

Co, Cu, Fe, Mn, Ni, Pb and Zn contents, both in total and partial extractions, have been determined for intertidal and foreslope surficial sediments of the Fraser River active delta-front. In conjunction with analysis of subsurface sediments and water and suspended sediment from the main channel, these data suggest controls on metal contents and distribution.

An inverse relation between total metal contents and sand content of sediment is demonstrated in geographic distributions and correlation analysis of metal data. Relatively greater concentrations of metals in hydrous oxide phases and detrital minerals of the silt-plus-clay fraction account for this relationship. Trace metals in heavy minerals of the sand fraction partially negate the grain-size effect. Adsorbed metals are an insignificant quantity (excepting Mn) except in two samples from an area receiving effluent from the Iona Island sewage treatment plant.

Variation of trace metal contents in short cores is generally related to transitions in sediment texture. Some metal may be mobilized and lost subsequent to burial, although this conclusion is contingent on the assumption that trace metal input to delta-front sediments is constant over time. One core collected near Iona Island, however, contains evidence that this assumption is not totally valid.

Scavenging of Zn, and probably other trace metals, by newly-formed hydrous Fe (and possibly Mn) oxides takes place in brackish conditions within the main channel. In conjunction

with physical processes which increase residence times of sediments in the estuarine portions of the river, this process accounts for removal of a sizeable fraction of dissolved metal.

Desorption of trace metals occurs in the channel and in Georgia Strait, although probably to a somewhat lesser extent than the sorption process.

In terms of metal contents and mechanisms of metal deposition, the Fraser delta-front is typical of nearshore sediments of low clay content. Trace metal sorption by various mechanisms, including that described here, accounts for retention of river-borne and waste metals in nearshore sediments.



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## CHAPTER I: INTRODUCTION

### Introduction

Deltaic and estuarine environments, despite their biological importance and vulnerability to contamination, have only recently begun to receive the attention of sedimentary geochemists. Studies of trace metal behaviour in these regions are vital to our understanding of biogeochemical cycles, for many changes in metal form and phase can be observed in these transition zones. Such changes affect availability of metals to organisms and food chains, and also determine, in conjunction with physical processes, geographic distributions and residence times of metals in the nearshore environment.

Sediments act as temporary sinks for trace metals, and thus their metal content reflects physical, chemical and biological processes affecting metal behaviour. In particular, they reflect processes which remove metals from the dissolved phase, and processes of sediment transportation and deposition. Since the bulk of river-borne dissolved metals is removed from solution in or near estuaries (Chester, 1965; Turekian, 1971) and since the majority of marine sediments are deposited in nearshore regions near river mouths, delta-front sediments are an ideal subject for marine metal-sediment interaction studies.

The Fraser delta is an ecologically and economically important region. Pressures of urban expansion and industrial development have altered or threaten to alter natural balances and necessitate detailed study of all aspects of the chemical, biological and physical environments. This study of trace metal



distributions and forms in delta-front sediments will, it is hoped, be useful to scientists and administrators concerned with the Fraser delta region.

### Review of Previous Work

Papers reporting total metal contents of nearshore sediments are common. For example, unpolluted sediments from Conception Bay (Slatt, 1974) display strong correlations between total trace metal contents and clay and organic-carbon content. Concentrations of total Co, Cu, Fe, Mn, Pb and Zn (but not Ni) in Solway Firth sediments (Perkins et al, 1973) are similarly correlated with fine-grained material.

Studies which attempt to extract various phases of metal from sediment are more rare. Chester and Stoner (1975) treated sediments from the Severn estuary with hydroxylamine-hydrochloride in acetic acid to extract adsorbed metals and those associated with iron and manganese oxides. They found that the metals most concentrated in the extract are Mn, Pb and Zn. A complex chemical fractionation of Los Angeles Harbour sediments was carried out by Gupta and Chen (1975). The phases extracted include dissolved (interstitial water), water-soluble, exchangeable, carbonate, easily reducible, organic and sulphide, moderately reducible, and lithogenous. Exchangeable metals comprise non-detectable or insignificant proportions of total metals, while lithogenous metals (those within detrital minerals) are the major fraction of Cu, Fe, Mn and Ni, but not Pb and Zn. Large proportions of the latter two metals are bound in amorphous Fe and Mn

oxides.

Transport of metals in rivers and through estuaries has received considerable attention in recent years. Gibbs (1973) investigated mechanisms of trace metal transport in the Amazon and Yukon Rivers. Metals were found to exist predominantly in detrital suspended particles and in amorphous coatings of iron and manganese oxides, with dissolved metals also constituting a significant proportion.

River-borne dissolved iron is removed from solution in several estuarine regions including the Gulf of St. Lawrence (Bewers et al, 1974), Saguenay fjord (Yeats and Bewers, 1976), the Beaulieu estuary (Holliday and Liss, 1976), the Merrimack estuary (Boyle et al, 1974), the Mullica estuary (Coonley et al, 1971) and three Puerto Rican estuaries (Lowman et al, 1966). Removal of iron was not observed in the Rhine estuary (Eisma, 1975).

Manganese in Naragansett Bay (Graham et al, 1976) and the Columbia estuary (Evans and Cutshall, 1973) is mobilized from sediment at low salinities, and, in the former case, is in turn removed from solution at higher salinities. Removal of dissolved manganese has been inferred in three Puerto Rican estuaries (Lowman et al, 1966). Manganese in the Beaulieu estuary behaves conservatively (Holliday and Liss, 1976), that is, no loss or gain of dissolved manganese occurs, other than that accounted for by mixing of fresh and saline waters.

Dissolved zinc concentrations also behave conservatively in the Beaulieu estuary (Holliday and Liss, 1976), and the Gulf of St. Lawrence (Bewers et al, 1974), whereas removal of dissolved zinc has been reported beneath the halocline of an Alaskan fjord

(Burrell, 1973), and has been inferred in three Puerto Rican estuaries (Lowman et al, 1966). Mobilization of zinc at low salinities has been reported using dissolved zinc data of the Var estuary (Fukai et al, 1975) and the Columbia estuary (Evans and Cutshall, 1973). Zinc concentrations in bottom sediments of the Rhine and Ems estuaries (de Groot, 1973) also imply mobilization.

Other trace metals have been reported to behave conservatively in the Gulf of St. Lawrence (Bewers et al, 1974), to be removed from solution in Long Island Sound (Schutz and Turekian, 1965) and three Puerto Rican estuaries (Lowman et al, 1966), and to be mobilized in the Rhine and Ems estuaries (de Groot, 1973).

Knowledge of metal behaviour in the Fraser delta and estuary region and southern Georgia Strait is rather sparse. Bottom sediments and water of the Fraser River near its mouth have been reported to contain contaminated levels of trace metals (Hall et al, 1974; Hall and Fletcher, 1974). Benthic organisms on Sturgeon Bank contain higher concentrations of trace metals than similar organisms from Roberts Bank and other locations in British Columbia (Parsons et al, 1973). Uptake of particulate iron by algae in Georgia Strait and subsequent release of dissolved iron was inferred by Williams and Chan (1966) to explain seasonal variations in these quantities. Desorption of zinc and copper from Fraser River freshet sediment in Georgia Strait was observed by Thomas (1975).

## Objectives and Outline of Study

The overall purpose of this study is to determine factors which control contents and distribution of Co, Cu, Fe, Mn, Ni, Pb and Zn in surficial sediments of the Fraser River active delta-front. Specific objectives are:

- i) to determine contents and distribution of metals in surficial sediment, and the chemical and physical sediment fractions in which the metals are bound;
- ii) to determine subsurface metal profiles in delta-front sediments; and
- iii) to detect changes in metal association in the estuarine portion of the main channel, particularly sorption and desorption reactions.

These objectives served as a framework for the study, and thus organization of this report follows a similar outline. After brief descriptions of the study area (Chapter II) and field and analytical techniques (Chapter III), results and discussion of study of surficial sediment metal contents and distribution are presented (Chapter IV). Chapter V presents results of total metal determination in short cores, and discussion of factors influencing metal profiles in subsurface sediments. Chapter VI discusses data of dissolved and suspended particulate trace metals in the estuarine portion of the Fraser River. Possible importance of processes observed in the Fraser estuary and delta-front to other regions and to the overall retention of metals in nearshore zones is discussed in Chapter VII. A brief summary of conclusions and some recommendations for further research follow in Chapter VIII.

## CHAPTER II: DESCRIPTION OF STUDY AREA

### Introduction

The Fraser River, with a length of 1370km and a drainage basin area of 234,000sq.km, is British Columbia's largest river (Fig. 1). Over most of its length the river flows through rugged terrain composed of volcanic, plutonic and sedimentary rocks, and glacial deposits (Garrison et al, 1969). The last 130km, the broad lower Fraser valley, is underlain by unconsolidated Pleistocene and Recent sediments of glacial, alluvial, littoral and deltaic origin (Armstrong, 1956).

At New Westminster, 24km above the mouth, the Fraser passes through a gap in topographically high Pleistocene deposits into the region of its modern delta (Johnston, 1921) (Fig. 2). The modern (or Recent) delta represents a period of deposition during which relative levels of sea and land have remained nearly constant, estimated independently as 8000 years (Johnston, 1921) and between 7,300 and 11,000 years (Mathews and Shepard, 1962). The delta is composed of alluvial and marine deposits and peat, and includes present and former distributary channels, channel bars, floodplains, marshes, tidal flats and fore-slope (Fig. 2). The seaward-facing perimeter is 48km and includes the active (western) delta-front which extends from Point Grey to the Point Roberts peninsula (a former island), and the inactive (southern) delta-front within Boundary Bay. The active delta-front, subject of this study, is prograding westward into Georgia Strait.

Topset sediments cover the tidal flat and salt marsh

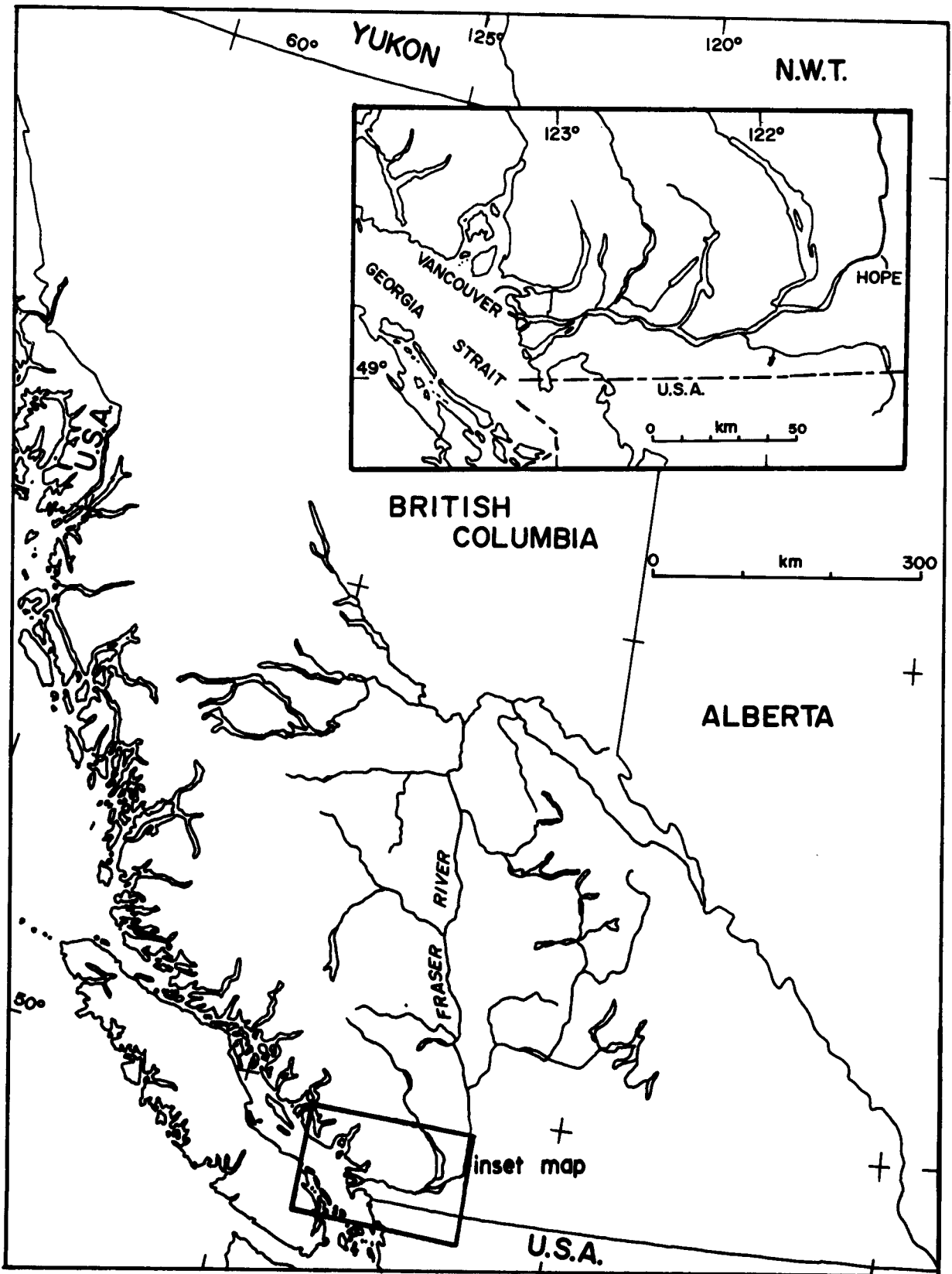


Figure 1: British Columbia and lower Fraser valley (inset), showing the Fraser River and major tributaries and distributaries.

# THE FRASER RIVER DELTA WITH GENERALISED SURFICIAL GEOLOGY

0 km 5

## LEGEND

### RECENT

- R<sub>1</sub> peat ± silt cover
- R<sub>2</sub> silt and clay
- R<sub>3</sub> sand
- R<sub>4</sub> salt marsh
- R<sub>5</sub> other

### PLEISTOCENE

- P sandy to silty till, sands, gravels, silt, clay and peat

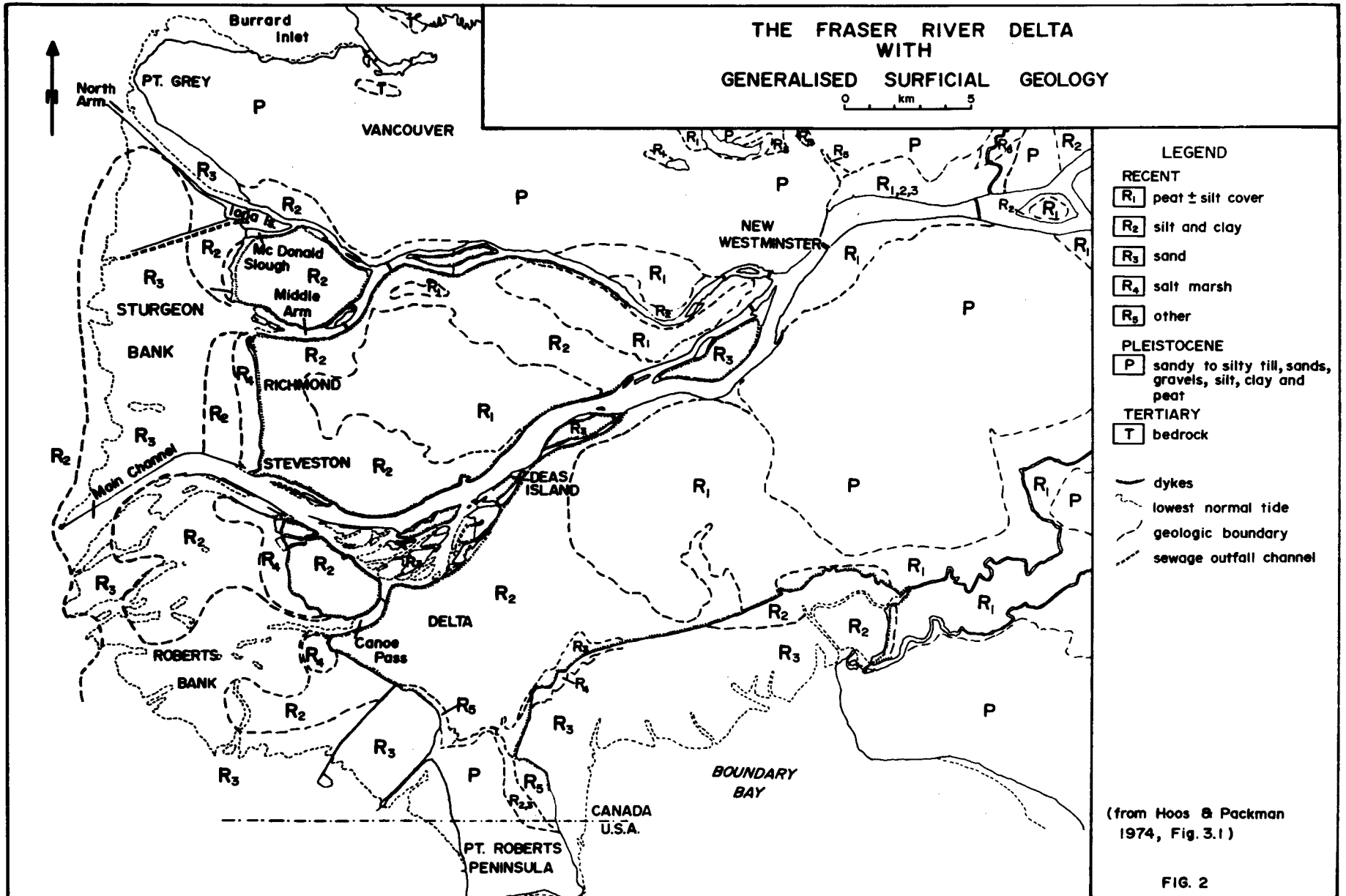
### TERTIARY

- T bedrock

- dykes
- - - lowest normal tide
- - - geologic boundary
- - - sewage outfall channel

(from Hoos & Packman  
1974, Fig. 3.1)

FIG. 2



zones, which slope only very gradually ( $0.04^{\circ}$  or .7m in 1km) over a distance of 7km. Two intertidal banks, Sturgeon and Roberts Banks, lie, respectively, north and south of the main channel (Fig. 2). Foreset beds cover the remaining width of Georgia Strait west of the first break in slope (Mathews and Shepard, 1962). Steepness of the fore-slope varies, although it is everywhere steeper than the tidal flats. Inclinations averaging  $1\frac{3}{4}$  to  $3\frac{1}{2}^{\circ}$  occur adjacent to the mouth of the river (Mathews and Shepard, 1962) and local values of  $12^{\circ}$  (Luternauer and Murray, 1973) and  $10^{\circ}$  (Johnston, 1921) have been documented.

### Hydrology

The Fraser River, near its mouth, has a mean daily flow of  $3400\text{m}^3/\text{sec}$  (Hoos and Packman, 1974). Nearly 80% of the annual total is discharged during the freshet months of May through July (Fig. 3), and the monthly mean for June is  $7075\text{m}^3/\text{sec}$ . Winter discharges, on the other hand, are much lower. March for instance has a mean discharge of  $790\text{m}^3/\text{sec}$ . Maximum daily discharges during the freshet have occurred in excess of  $15,000\text{m}^3/\text{sec}$ , and account for periodic flooding over the alluvial plain of the delta. The banks of distributary channels are dyked to prevent flooding of populated regions.

The river enters Georgia Strait through four main distributary channels (Fig. 2), the approximate proportion of discharge carried by each being: main channel, 80-85%; Middle Arm, 5%;



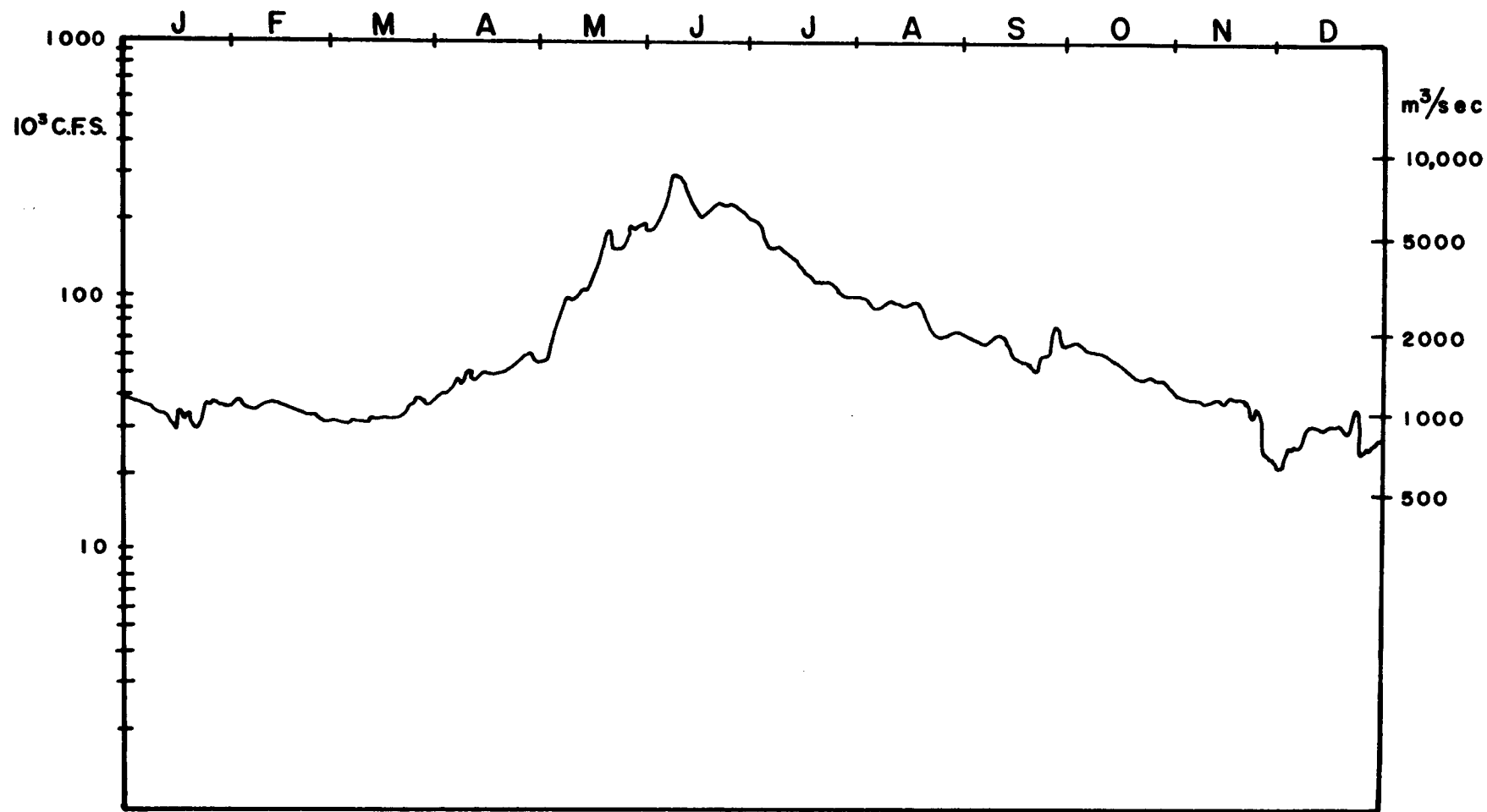


Figure 3: Discharge hydrograph for 1970, Fraser River at Hope (Hoos and Packman, 1974)

North Arm, 5%; and Canoe Pass, 5-10% (Pretious, in Luternauer and Murray, 1973).

### Oceanography

The physical oceanography of Georgia Strait has been summarized by Hoos and Packman (1974), Waldichuk (1957), and Thomson (1974a, 1975). Most of the following information is drawn from these sources.

#### Tides

Tides in Georgia Strait are a mixture of diurnal and semi-diurnal types, with a marked diurnal inequality. In other words, two unequal high tides and two unequal low tides occur daily, and times between successive equivalent states of tide vary. Average tidal range in Georgia Strait is 3m, and range of spring tides averages 4.6m. Tidal heights are defined relative to zero chart datum (lowest normal tide) and are affected by river discharge only near the mouth of the main channel (Ages and Woollard, 1976).

Highest normal tides cover the entire active delta-front, with waters lapping against dykes along shorelines of Richmond and Delta (Fig. 2). At lowest normal tide water recedes 6 to 7km, within 1km of the first distinct break in slope.

Water levels in the lower Fraser River are influenced by tides, amount and extent of their influence being determined by tidal state and river discharge (Ages and Woollard, 1976). During low flow periods, tidal influences are felt up to 72km

upstream. New Westminster (24km upstream) has a maximum tidal range of nearly 1m. During the peak freshet flows, however, tidal effects extend only a short distance upstream of Steveston, being overpowered by the river flow. Tidal extremes are progressively delayed moving upriver, by amounts not generally affected by discharge (Ages and Woollard, 1976). Model predictions of tidal delay (Ages and Woollard, 1976) suggest low tides are delayed one hour and two hours at Deas Island and New Westminster respectively, and high tides are delayed twenty minutes and one hour.

### Surface Currents

Surface currents in Georgia Strait near the delta-front are influenced primarily by tides and Fraser River discharge. Tidal currents in general ebb to the southeast and flood to the northwest, the flood tide being the stronger. However, drogue studies near the mouth of the Fraser (Giovanda and Tabata, 1970) indicate that actual flows are to the southwest during the ebb, swinging to due north on the flood. The southwestward ebb flow is in part due to the force of Fraser River water entering the strait, and to Coriolis effects acting on brackish surface water. The northerly flood is due to Coriolis effects, although near the river mouth the river dominates, producing a short southwestward-directed flow. Adjacent to Sturgeon Bank a northward-directed surface current flows at all states of tide. This current is believed to be caused by internal waves breaking at shallow depth near the edge of the tidal flats (Thomson, 1974b). Currents near

the mouth of the North Arm are northwestward, veering around Point Grey and into Burrard Inlet on the flood.

Currents over the intertidal banks of the delta are produced by flooding and ebbing tides and are roughly at right angles to the shore. The flood tide is the stronger and therefore shoreward currents are more powerful than seaward currents.

Surface current magnitude and direction at the river mouth and in distributary channels are dependent on river flow and state of tide. Downstream velocities in the main channel are normally 3 to 4 knots during ebb tide, but may reach 5.5 knots during the freshet (Tabata, 1972). On flooding tides surface speeds are considerably reduced, and actually reverse at most times of the year, often as far upstream as New Westminster.

#### Interaction of Fraser River and Georgia Strait Waters

Sediment-laden river water, because of its lower density, spreads over the surface of Georgia Strait in a turbid plume, where its movement is determined by factors which control surface currents. Mixing between fresh and saline waters occurs only at their interface, with a loss of saline water to overlying river water. A two-layered estuarine system thus develops with overlying brackish water outflow and saline subsurface inflow (Waldichuk, 1957). The relatively tranquil waters of central Georgia Strait allow the two-layered system to persist.

A two-layered system exists also in the main channel of the Fraser due to a wedge-shaped intrusion of saline water along the base of the channel. Penetration distance is dependent

on discharge, state of tide, and difference between successive tidal heights. During the winter penetrations greater than 15km have been recorded (Hodgins, 1974), while during the freshet the saline wedge probably never passes Steveston (Pretious, 1972). On the large ebb of every tidal cycle the saline water is completely flushed out of the main channel (Hodgins, 1974). The halocline associated with the salt wedge is not as well defined as that in well stratified estuaries: a certain amount of two-way mixing between layers occurs, along with upstream convection of brackish Georgia Strait surface water on flooding tides (Hodgins, 1974).

Penetration of the saline wedge generally lags two or three hours behind arrival of high tide (Hodgins, 1974). Consequently velocity gradients are common within the channel, and, in extreme cases, surface and bottom waters flow in opposite directions.

### Sedimentology

#### Sediment Transport in the Fraser River

The Fraser transports an average of  $1.98 \times 10^7 \text{ m}^3$  of sediment to the delta-front each year (Mathews and Shepard, 1962). All material destined to reach the delta-front is probably in suspension at Hope (Mathews and Shepard, 1962), but a large proportion of the annual load has settled out upstream of Steveston (Milliman, in press). Material settling out of suspension is mainly sand, as evidenced by the small proportion of silt and clay in river bottom sediments upstream of Steveston (Tywoniuk, 1972). Bed-load sands in the tidally affected portion

of the river are subject to resuspension during ebb tide (Milliman, in press). This effect is particularly noticeable in the lowermost reaches of the river where resuspension of sand causes a turbidity maximum. Silt and clay content of the water column, in contrast, is relatively constant with respect to position, tide and depth in the lower reaches of the river, although on some occasions a slight increase in suspended silt and clay may reflect resuspension (Milliman, in press). A turbidity maximum of continuously suspended silt-plus-clay has not been demonstrated, although the two-layer flow system (p. 14) might produce such a maximum near the toe of the salt wedge, as observed in other stratified estuaries (e.g., Schubel, 1968).

Quartz, feldspar, chlorites and micas were identified by x-ray diffraction of suspended sediments collected during this study. Visual analysis of filters identified large quartz and biotite grains.

#### Sediment Distribution on the Active Delta-Front

Luternauer and Murray (1973) have described sedimentary environments within the study area.

The salt marsh (Fig. 2) is a 1km-wide flat to hummocky region of fine sediment lying near high tide level (Luternauer and Murray, 1973). It is characterized by a dense salt-tolerant vegetation cover during spring and summer. Sediments, where undisturbed, show distinct alternating laminations of fine sand and mud (Plate 1) on a scale of five pairs per cm (Johnston, 1922). Very likely, fine sand laminations represent material sett-

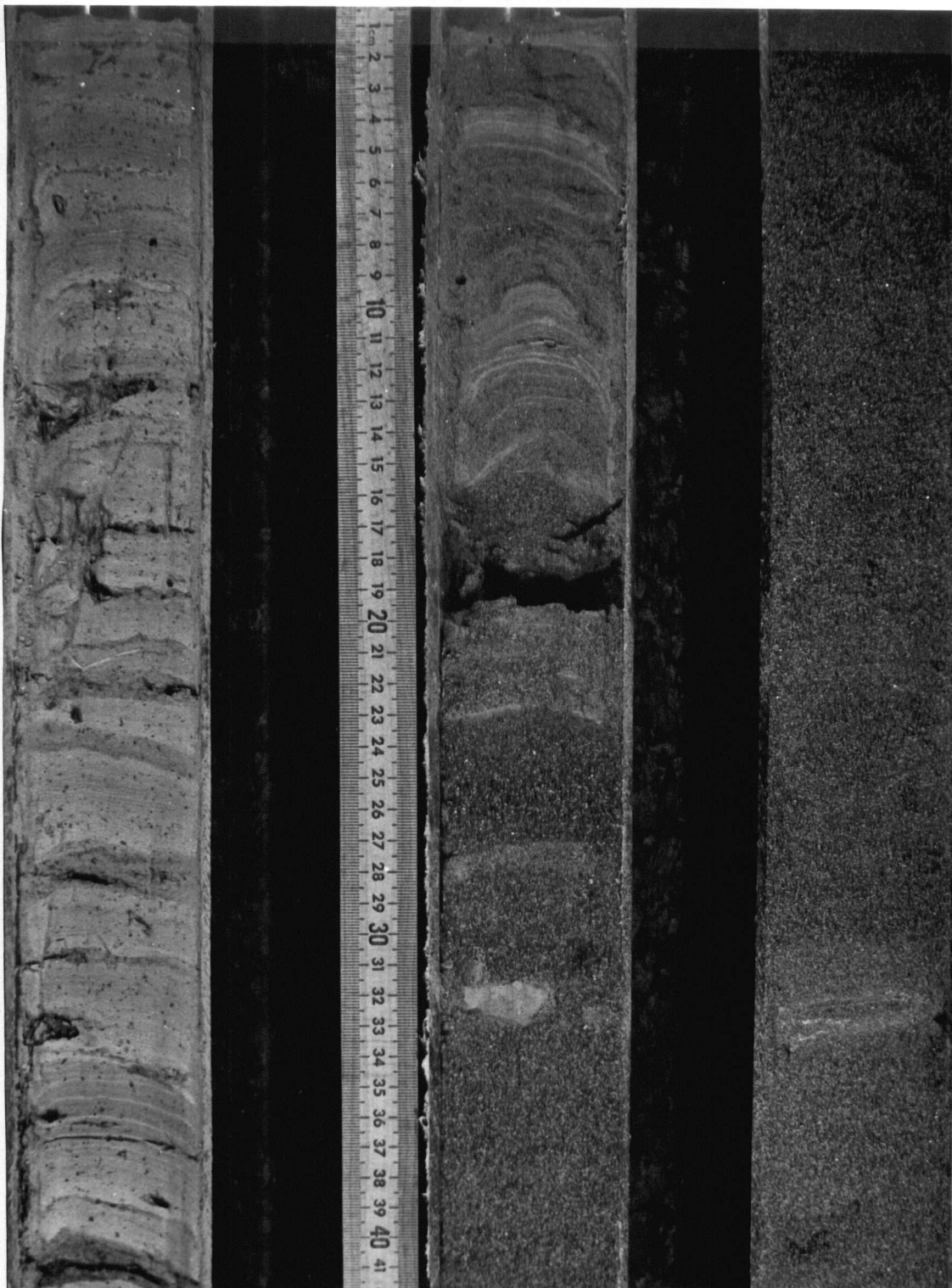


Plate 1: Upper portion of Cores 34, 38 and 16 (left to right) collected from three contrasting environments on Roberts Bank. Metal contents of cores are displayed in Fig. 17.

ling on the strong flooding tides, while muddy laminations are deposited at slack water. Unfortunately annual or seasonal sedimentation rates are not available to test this theory.

Tidal flats extend seaward from the marsh to the line of lowest normal water level (Fig. 2). They are covered by fine sand and silt, and, especially adjacent to Middle Arm and Canoe Pass and near low tide line, by medium grained sand (Luternauer and Murray, 1973). Tidal flats are featureless except for shallow tidal channels and hydraulic bedforms (Medley and Luternauer, 1976). Sediment cores lack distinctive layering (Plate 1), because constant current, wave, channeling and burrowing action tends to destroy their stratigraphy.

A facies succession of salt marsh muds over tidal flat sand is typical in regions where the salt marsh is advancing (see Plate 1). Fluctuation of environmental conditions from year to year leads to alternating mud and sand interlayers.

Sediments of the upper fore-slope of Sturgeon Bank are considerably finer than tidal flat sediments (Fig. 2) and decrease in size to the west. The same is true west of the northern portion of Roberts Bank. To the south, however, the fore-slope is mantled with sand well into deep water (Luternauer and Murray, 1973). It appears that northward-trending internal wave-generated currents and flood tidal currents (p. 12) move the plume north from the main channel, restricting supply of suspended sediment to the Roberts Bank fore-slope. Alternately, subsurface currents of unknown nature may prevent deposition of sediment in this region, and may contribute to the erosion and retreat of this part of the delta-front (Mathews and Shepard, 1962; Lutern-



auer and Murray, 1973; Luternauer, 1975a).

The clay content of sediments of the study area is generally low, reaching an average maximum of 30 to 40% in stations furthest offshore from the Sturgeon Bank fore-slope (Luternauer, unpublished data). Muddy salt marsh samples from Roberts Bank contain over 20% clay, but other salt marsh and tidal flat sediments contain little or no clay. Much of the clay-size material, however, may be finely ground rock-forming phyllosilicates rather than pedogenically formed minerals. Pharo (1972), for example, has inferred that clay-size 'illite' in Georgia Strait is finely ground mica.

Mineralogy of some delta-front sediments was investigated by MacKintosh and Gardner (1966). Silt fractions were found to contain quartz, feldspars, micas, chlorites, amphiboles and pyroxenes, with non-phyllosilicates more prominent in the coarse subfraction. Clay fractions contain montmorillonoid minerals, chlorites and micas, with mixed-layer chlorite-montmorillonite, quartz and feldspars in the coarse subfraction. The silt fraction of Georgia Strait sediments was found by Pharo (1972) to contain micas, quartz, chlorites, feldspars and amphiboles. All these minerals plus montmorillonite are found in the clay fraction, the last mineral being dominant in the finest subfraction. Minerals of the silt-plus-clay fraction of samples analysed in this study include quartz, feldspars, chlorites and micas, and minor amphiboles.

Average composition of delta-front sands was reported as 40% quartz, quartzite and chert, 11% feldspars, 45% unstable rock fragments (mainly volcanics) and 4% miscellaneous detritus (Garrison et al, 1969). However, visual inspection of sands collected in this study shows that amphiboles, epidote, chlorites, micas and magnetite are common constituents.

### Environmental Considerations

Environmental knowledge of the entire Fraser River delta and estuary has been summarized by Hoos and Packman (1974). This work should be consulted in regard to ecosystems and environmental problems of the delta-front.

As do most estuarine areas, the Fraser delta-front hosts an extremely complex and prolific biota. The proximity of major urban and industrial centres such as Vancouver and New Westminster renders the region susceptible to environmental contamination, and consequent introduction of foreign substances to ecosystems and food chains. The lower levels of the food chains include plants and minute crustaceans, with fish, birds and man occupying the upper trophic levels. Of particular concern is a multi-million dollar fisheries industry, whose curtailment would drastically affect regional economy.

Trace metals are waste products of many local activities, including petroleum use and chemical industries, and are known to occur in lower Fraser River water and sediment in higher than normal concentrations (Hall and Fletcher, 1974;

Hall et al, 1974). Lead and zinc concentrations in unfiltered waters from the vicinities of New Westminster and Annacis Island have been recorded in excess of 30 and 70ug/l respectively (Hall et al, 1974). The Greater Vancouver Regional District primary sewage treatment plant at Iona Island (Fig. 2) is supplying a further input of metals to the delta-front. Waste received by this plant contains median Cu, Pb and Zn concentrations of 105, 39 and 108ug/l respectively (Hall et al, 1975).

Metal associated with sediment enters food chains through filter-feeding and sediment-ingesting organisms, and marsh vegetation. Crabs and molluscs from Sturgeon Bank, for example, contain greater concentrations of several metals than those from Roberts Bank (Parsons et al, 1973), probably as a result of effluent discharged from Iona Island. Copper concentrations, for example, range from 38 - 150ppm in animals from Sturgeon Bank, and from 22-68ppm in animals from Roberts Bank (Parsons et al, 1973).

## CHAPTER III: SAMPLING AND ANALYTICAL PROCEDURES

Sample CollectionSediments

The surficial sediment sampling programme, planned and supervised by Dr. J.L. Luternauer of the Geological Survey of Canada, was designed to provide a monthly record of the dispersal of sediments over the active delta-front before, during and after the freshet of 1974 (Luternauer, 1975b). Tidal flats were sampled during February, April, May, June and October. Upper fore-slope sediments were collected in March and October, for a total of 691 samples. Locations of samples collected in February and March, 1974 are shown in Fig. 4.

Tidal flats were sampled at lowest tides from the Coast Guard Hovercraft stationed at Sea Island. A regular grid of 70 stations was planned, but could not be rigidly adhered to, as accessible topographic highs shift constantly across the sand flats. Locations were determined to within 30m using the craft's Decca radar system. Sediments were collected using a glass petri dish to make a 10cm by 1cm disc of sediment. The sediment was slid onto a rigid vinyl sheet and placed in high wet strength kraft bags.

Upper fore-slope sediments were sampled from a Department of Transport launch along east-west transects using a Shipek sampler with a stainless steel bucket. Only the upper few centimetres of the grab were placed in sample bags. Locations were determined to within 10m using a Trisponder navigational system.

Sediment cores were collected from exposed parts of

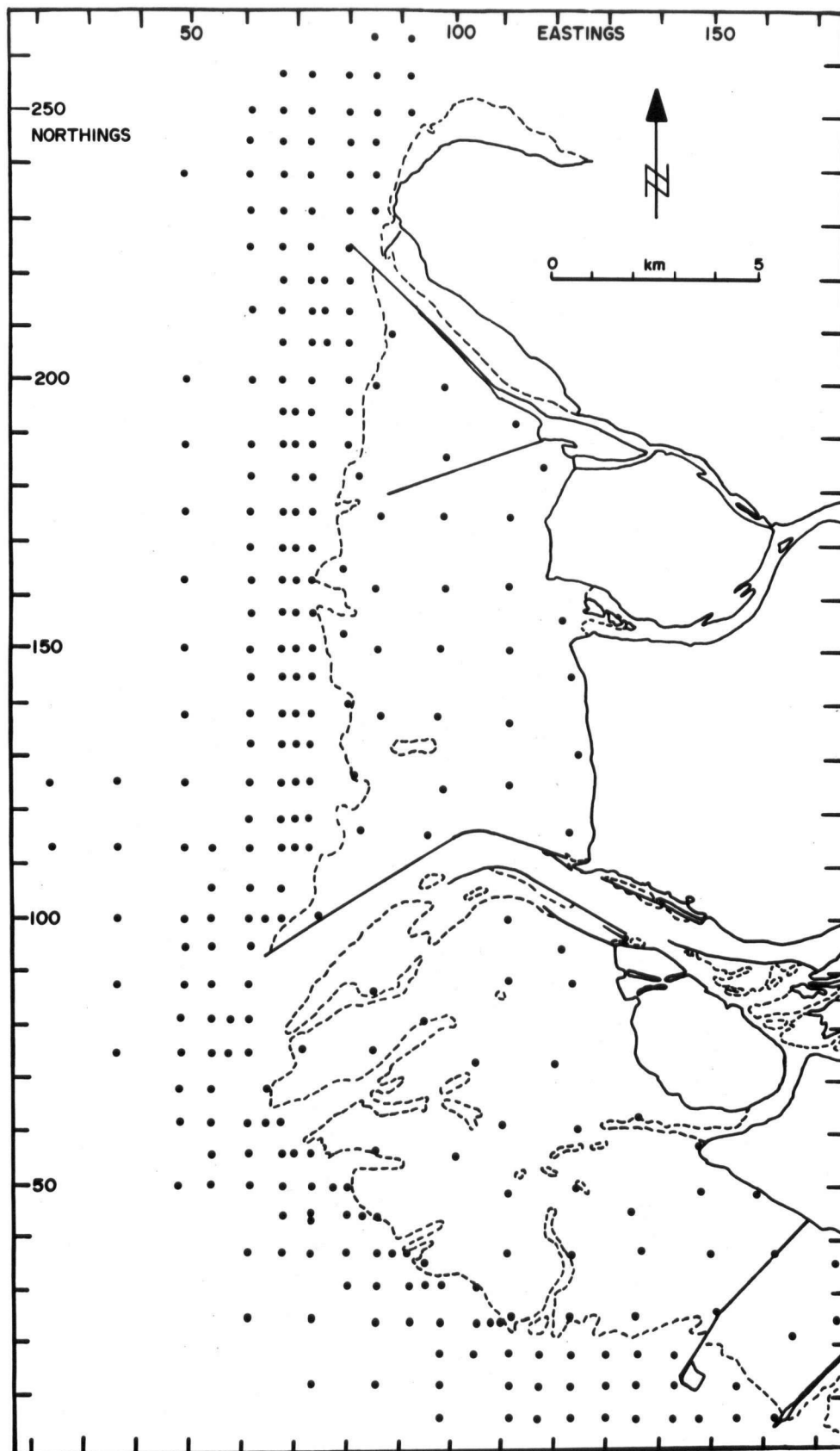


Figure 4: Locations of surficial sediment samples (February and March sampling series), Fraser delta-front intertidal and fore-slope regions (origin of coordinates at 49°00'N, 123°25'W).

the tidal flats during the summer of 1975 (Fig. 5). Dykes and causeways provided access to several localities. Other stations were reached by Canova boat via river and tidal channels. Cores were extracted far enough away from man-made barriers to be unaffected by material washed out of fill.

Cores of roughly 70 to 80cm length were extracted by pounding a 6cm i.d. PVC core liner into the sediment. A PVC piston (Fig. 6) was held at the same level as the liner was intruded, to prevent compaction. A rubber disc near the top of the piston acted as an air seal, thus maintaining a vacuum within the liner and allowing successful extraction of the sediment. Cores were capped and transported vertically back to the laboratory where the liner was cut length-wise with a circular saw. A stainless steel spatula was inserted through the split liner and drawn through the core. One half of the core was then divided into 5cm subsamples after the top 1cm and a few millimeters of the outside surface had been discarded. Subsamples were placed in kraft bags, while the other half of the core was saved for description and photography.

### Waters

On August 19, 20 and 21, 1975 water samples were collected from 1m depth at eight stations on the Fraser River from the UBC Geological Sciences Department motorboat Nautilus. Samples were collected with the boat facing upstream using a van Dorn sampler. At each station water was poured into two 2l polypropylene aspirator bottles which had been previously washed with 50%

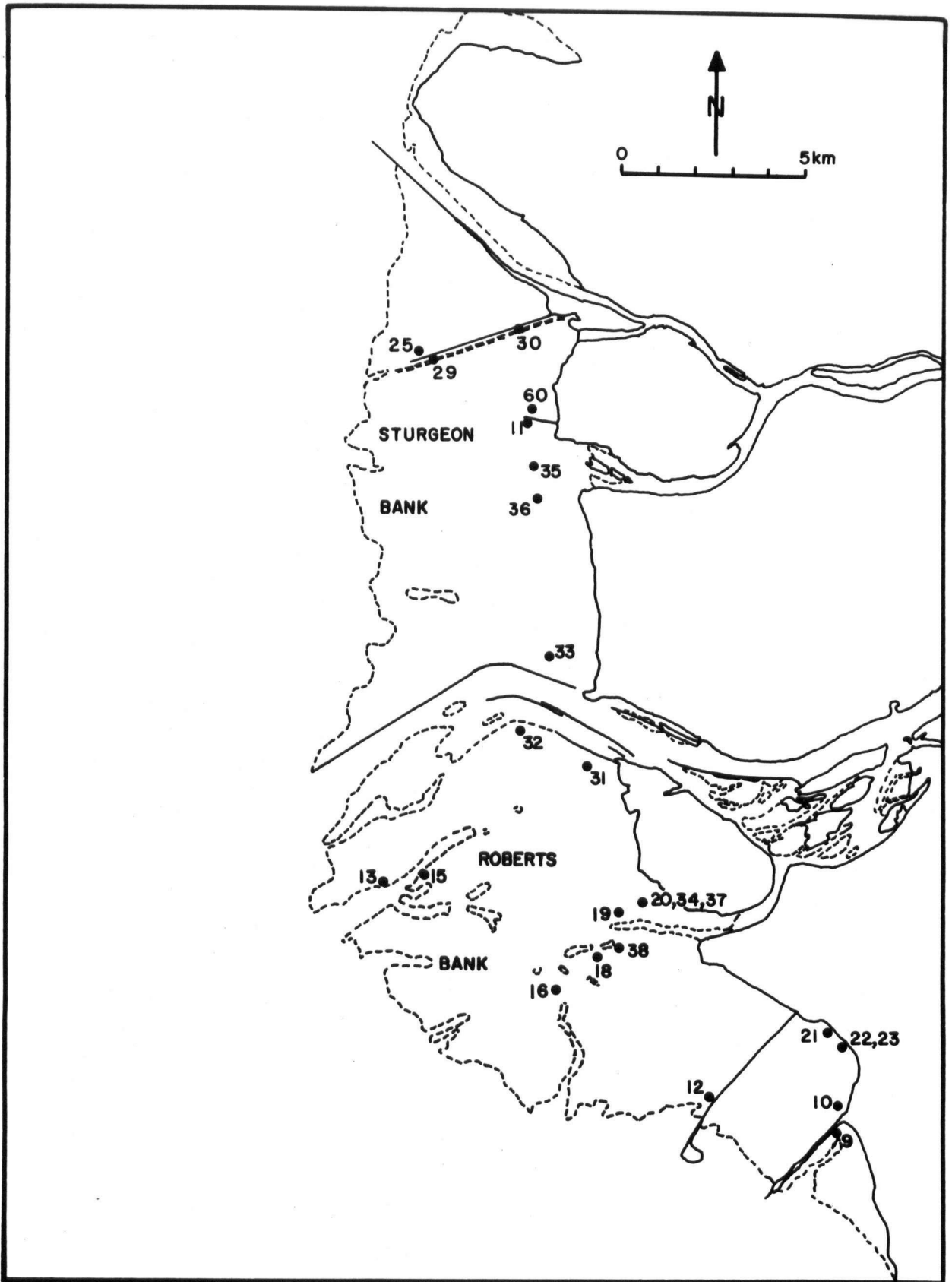


Figure 5: Locations of intertidal sediment short core samples.

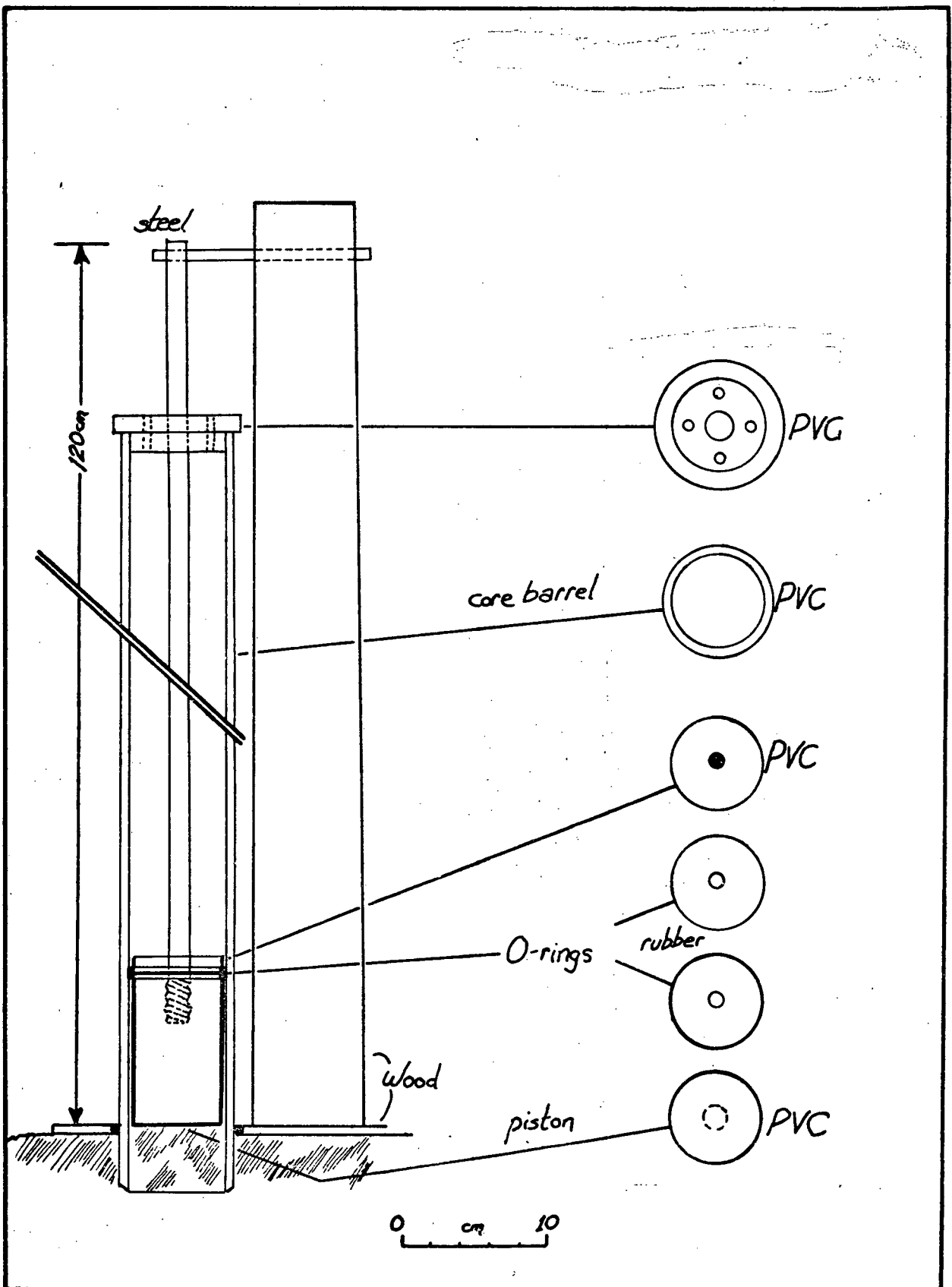


Figure 6: Diagram of sediment coring device used in this study.



HCl and rinsed with distilled water. Water conductivity was measured in situ with a Hydrolab probe conductivity meter. At stations 3, 4 and 5 steep salinity gradients were detected with increasing depth. Additional water samples were taken at these locations at a depth of relatively constant salinity, apparently within the zone of salt water intrusion. Samples were taken immediately back to the laboratory for filtration.

### Sample Preparation

#### Sediments

Surface samples and core subsamples in kraft bags were air-dried at 70°C for at least 48 hours. Dried material was disaggregated with a ceramic mortar and pestle. Portions of each sample were then passed through a nylon sieve to produce fractions coarser and finer than 80-mesh or 177µm (plus80 and minus80-mesh). Sieved material was placed in coin envelopes and the remainder of the sample left in the kraft bags.

#### Waters and Suspended Sediments

On returning to the laboratory water in aspirator bottles was filtered under N<sub>2</sub> pressure through preweighed .45µm Sartorius membrane-filters. The first 100ml of filtrate was discarded, after which acid-washed 1l polybottles were used to collect filtrate. One-litre bottles were rinsed with a small amount of filtrate before filling them. Distilled-deionized water was passed through the filters when filtration was complete. Two filters

were used per sample, one for each 2l aspirator bottle. Filtered waters were acidified with 5ml concentrated HCl and stored at 4°C.

Filters were placed in separate dust-free plastic dishes in a dessicator and allowed to dry at room temperature before reweighing to estimate weight of particulates. To test for filter weight changes during filtration 2l of distilled water was forced through each of eight pre-weighed filters, four of which were allowed to dry in a dessicator, four in a drawer. Significant weight loss (3mg) occurred in only one case. No correction was made therefore for changes in filter weight.

### Trace Metal Analyses

#### Sediments

Metal extraction Several extraction procedures were used to liberate different forms of trace metals from sediments. Perusal of the literature suggested many alternate combinations of reagents to isolate various chemical fractions.  $\text{MgCl}_2$  was chosen to separate adsorbed metals rather than ammonium acetate, the usual cation exchange determinant, because ammonium acetate has been found to dissolve iron oxide grain coatings (Gibbs, 1973). Moreover  $\text{Mg}^{++}$  is a major ion in the marine environment, making the experiment somewhat closer to real conditions. Whether this reagent releases all adsorbed metal, or only that in cation exchange position, is unknown.

1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% acetic acid (HHA) was selected as the most suitable reagent to separate metals associated with amor-

phous iron and manganese oxides (Chester and Hughes, 1973). High rate of recovery with minimum destruction of clay mineral lattices and crystalline iron oxides have been reported with this reagent.

Combined acid attacks ( $\text{HNO}_3\text{-HClO}_4$  and  $\text{HF-HNO}_3\text{-HClO}_4$ ) are known to liberate the bulk of metals bound in crystalline minerals, yielding near-total metal contents when used without preceding extractions.

Experimental procedures are outlined below.

*Digestion with  $\text{HNO}_3\text{-HClO}_4$ :* This was the routine procedure used to liberate the bulk of lattice-bound metals and obtain near-total metal contents of sediments. A 2ml aliquot of 4:1  $\text{HNO}_3\text{-HClO}_4$  was added to 0.500g of dried sediment, and evaporated to dryness on a hot-air bath. The residue was dissolved in warm 6M HCl and the solution diluted to 1.5M for analysis. Necessary dilutions were made using 1.5M HCl.

*Sequential treatment with 1M  $\text{MgCl}_2$ , HHA and  $\text{HNO}_3\text{-HClO}_4$ :* To first remove adsorbed metals 2.500g of dry sediment was leached by shaking for four hours with 20ml 1M  $\text{MgCl}_2$ . The solution was then centrifuged and the supernatant solution analysed. After washing with distilled water the residue was shaken for four hours with 20ml HHA to remove amorphous oxides and hydrous oxides of iron and manganese, together with associated trace metals. One-half gram of the residue was then digested in  $\text{HNO}_3\text{-HClO}_4$  as described above.

*Sequential treatment with HHA and  $\text{HF-HNO}_3\text{-HClO}_4$ :* Minus80-mesh sediments were split into sand (plus270-mesh) and silt-plus-clay (minus270-mesh) fractions using a nylon sieve. 4.000g of each

fraction was shaken for four hours with 40ml HHA to remove adsorbed and hydrous oxide-associated metals. The suspension was centrifuged and the supernatant solution was saved for analysis. The residues were washed with distilled water, and the sand fraction split into heavy and light fractions using bromoform (S.G.=2.89) in a separatory funnel. 0.200g of the heavy sand fraction and 0.500g of the light sand and silt-plus-clay fractions were digested in teflon dishes with 5ml HF and 2ml 4:1  $\text{HNO}_3\text{-HClO}_4$ . After evaporation to dryness on a hot plate, the residue was taken up in 6M HCl and then diluted to 1.5M with distilled water.

Atomic absorption spectrophotometry For analysis of above solutions it was necessary to prepare standard solutions in 1.5M HCl, 1M  $\text{MgCl}_2$  or HHA as appropriate.

Solutions were analysed on either a Varian Techtron IV or Perkin-Elmer 303 atomic absorption spectrophotometer, using an air-acetylene flame under conditions listed in Table I. Corrections for background absorption were made for Co, Ni and Pb using a continuum light source (Fletcher, 1970).

One set of duplicates, a standard sample and a reagent blank were included in every batch of 24 samples during  $\text{HNO}_3\text{-HClO}_4$  procedure. Precision, based on duplicate sample analysis, is tabulated in Table II. Precision of sequential extraction analyses, based on duplicate samples, is given in Table III. Generally poor precision for Pb reflects the high proportion of values approaching or below the detection limit of the methods.

### Suspended Sediments

After drying, one of the two filters used per sample was

<u>Element</u>	<u>Flame</u>	<u>Wavelength(<math>\overset{\circ}{\text{\AA}}</math>)</u>	<u>Current(mA)</u>	<u>Slit(<math>\mu\text{m}</math>)</u>	<u>Background Correction</u>
Co	Air-acetylene	2407	18 <sup>a</sup>	300 <sup>a</sup>	yes
Cu	"	3248	14(3) <sup>b</sup>	1000(50) <sup>b</sup>	
Fe	"	3719	20(5)	300(50)	
Mn	"	2795	15(5)	1000(50)	
Ni	"	2320	16	300	yes
Pb	"	2170	14	1000	yes
Zn	"	2139	14(6)	3000(100)	

a Perkin-Elmer 303

b Varian Techtron IV

Table I: Instrumental conditions of atomic absorption spectrophotometry.

<u>Element</u>	<u>Precision <math>\pm\%</math> (95% confidence)</u>
Co	10.3%
Cu	8.4
Fe	6.4
Mn	18.9
Ni	5.6
Pb	45.7
Zn	9.3

Table II: Analytical precision of  $\text{HNO}_3\text{-HClO}_4$  attack, based on analysis of 20 paired samples.

<u>Element</u>	<u>Precision <math>\pm\%</math> (95% confidence)</u>	
	<u>HHA-extraction</u>	<u><math>\text{HNO}_3\text{-HClO}_4</math>-extraction</u>
Co	*	62.8
Cu	4.2	8.2
Fe	19.9	5.3
Mn	6.6	4.1
Ni	17.8	17.8
Pb	8.5	92.6
Zn	20.8	6.9

\* not calculated.

Table III: Analytical precision of first sequential extraction experiment, based on analysis of 6 paired samples.

placed in a Teflon dish with 4ml 4:1  $\text{HNO}_3\text{-HClO}_4$  and 2ml HF and heated on a hot plate until dry. The residue was taken up in 6ml 6M HCl, and the solution poured into an acid-washed 25ml volumetric flask and taken to volume with distilled water. A 5ml aliquot of this solution was diluted 200 times with 1.5M HCl for analysis of Fe, Ca, Mg, Na and K. Diluted solutions contained 10ml .07M CsCl and .37M LaO solutions per 100ml to suppress interferences in determinations of Na and K, and Ca and Mg respectively. The remainder of the 25ml was analysed directly for Cu, Mn and Zn by atomic absorption.

The other filter from each sample was placed in an acid-washed 150ml beaker and immersed in 5ml HHA to remove adsorbed and hydrous oxide-associated metal. Beakers were agitated gently for four hours on a gyrating surface, and the liquid was poured into a 10ml volumetric flask and taken up to volume with HHA. Solutions were analysed directly for Fe, Mn and Zn by atomic absorption. HHA-leached filters were washed with distilled water and allowed to dry at room temperature for use in x-ray diffractometry.

### Waters

Dissolved Cu, Zn and Fe in filtered waters were analysed in the Water Quality Lab at B.C. Research using a chelation-solvent extraction method. 750ml of acidified filtered waters were adjusted to pH2.5 with redistilled HCl. 30ml of a 1% (w/v) solution of the complexing agent ammonium pyrrolidine dithiocarbamate (APDC) in deionized water was placed, along with the sample, in a

separatory funnel and shaken. After standing for 10 minutes the APDC was extracted and removed three times into, successively, 20ml, 10ml and 10ml of chloroform. Chloroform extracts were evaporated to dryness, and the residues digested in 5ml of concentrated  $\text{HNO}_3$ . After warming until brown fumes were no longer evolved, 10ml of deionized water was added and boiled until a clear solution was obtained. Solutions were made up to 25ml in a volumetric flask. Analyses were done by atomic absorption, using standards made from a mixture of extracted water samples (reextracted once more with 10ml chloroform) by spiking with mixed standards and extracting as above.

### Mineralogical Determinations

#### Surficial Sediments

Material finer than 270-mesh, previously treated with HHA and assumed to be effectively  $\text{NH}_4^+$ -saturated, was made into a slurry with distilled water and placed on a glass slide for x-ray diffraction. Subsequent to the first scan ( $3-25^\circ 2\theta$ ) samples were treated with two drops of ethylene glycol, and were allowed to dry at room temperature for one hour. After a second scan ( $3-14^\circ 2\theta$ ) samples were heated at  $300^\circ\text{C}$  for one hour in a muffle furnace and rescanned. A Philips x-ray diffractometer, utilizing  $\text{CuK}\alpha$  radiation at a potential and current of 40kv and 20ma, was employed. Mineral identifications were made by referral to Carroll (1970, Fig. 11 and Table 9) and Chao (1969).

Qualitative visual identification of sand-size material



was done under the binocular microscope.

### Suspended Sediments

Small portions of HHA-leached filters were cut with scissors and mounted directly on glass slides with Scotch tape. X-ray diffraction was carried out as described for surficial sediments. To heat, filters were placed in crucibles, and the resulting sediment flakes were disaggregated with mortar and pestle. Material was then sprinkled onto glass slides which were coated with a thin layer of silicone stop-cock grease.

### Grain Size Determinations

Weight percent of sand in the finer than 80-mesh fraction (%sand) of February and March surface samples and selected cores was determined by wet-sieving approximately 1g of sediment through a 270-mesh (53um) nylon sieve, then drying and weighing the fraction retained.

### Loss on Ignition

Organic content of the finer than 80-mesh fraction was estimated as percent weight loss on ignition (%LI) after heating 1.000g of sediment for four hours at 550°C in a muffle furnace. LI values have been shown to be proportional to organic carbon content in other environments (Coker and Nichol, 1975). Carbonate minerals are not destroyed at this ignition temperature (Timperley and Allan, 1974).

### Correlation and Regression Analysis

Correlation matrices and regression equations were computed using the UBC TRIP computer program (Bjerring and Seagraves, 1974). Significance of correlation coefficients at the 95% confidence level was determined from Table VIII of Sokal and Rohlf (1973). The stepwise multiple regression produces equations of the form

$$Y = b_0 + b_1x_1 + b_2x_2 + \dots + b_nx_n$$

where Y is a dependent variable,  $x_1, x_2, \dots, x_n$  are independent variables, and  $b_0, b_1, \dots, b_n$  are regression coefficients. Independent variables making a significant contribution at the 95% confidence level are retained in equations, and those making no significant contribution are eliminated. Values of  $r^2$ , the proportion of variability in the dependent variable accounted for by the independent variables, are produced. Residuals, the differences between values observed and those predicted by regression equations, are listed in actual and normalized form.

## CHAPTER IV: TRACE METALS IN SURFICIAL SEDIMENTS OF THE FRASER RIVER DELTA-FRONT

### Introduction

Surficial samples from intertidal and upper fore-slope regions of the Fraser River active delta-front were analysed for total contents of Co, Cu, Fe, Mn, Ni, Pb and Zn. Significant statistical correlations between metals and sediment texture suggested chemical and physical partitioning experiments useful to elucidate metal forms and associations in sediment.

### Results

#### Trace Metal Content and Distribution

Results of total Co, Cu, Fe, Mn, Ni, Pb and Zn analyses on minus80-mesh material are listed in Appendix A, and means and standard deviations for each sampling series are listed in Table IV. Mean values of metals in tidal flat samples do not differ significantly between sampling series. The February series samples are therefore taken to be representative of intertidal sediments, and most of the ensuing description is based on samples from that series together with the March series of fore-slope samples.

In general mean values of the metals studied here are higher in fore-slope samples than in intertidal samples (Table IV). This tendency applies to contents of Fe (15% higher), Zn

	Metal Content (ppm)								
<u>Sampling Series</u>	<u>Co</u>	<u>Cu</u>	<u>Fe(%)</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb<sup>a</sup></u>	<u>Zn</u>	<u>%sand</u>	<u>%LI</u>
<u>Intertidal</u>									
A February	11.3 <sup>b</sup>	17.2	1.86	310	43.5	5.8	52.8	81.6	1.8
(n=68)	1.6 <sup>c</sup>	7.7	0.27	56	7.8	9.1	11.0	21.6	1.0
C April	13.3	17.5	1.93	357	47.5	5.2	55.7		
(n=69)	1.9	10.1	0.33	75	12.1	5.5	14.9		
D May	14.1	20.4	2.09	390	47.7	6.1	58.0		
(n=70)	2.6	12.0	0.41	132	8.2	6.2	15.3		
E June	11.6	17.6	1.94	336	44.0	5.2	53.0		
(n=64)	2.0	9.9	0.37	105	7.9	4.8	13.6		
F October	12.3	13.7	1.74	337	44.0	6.7	47.5		
(n=46)	2.5	5.8	.30	245	7.6	3.6	8.4		
<u>Fore-slope</u>									
B March	13.3	30.0	2.34	327	47.9	10.7	77.1	45.5	3.5
(n=218)	1.8	13.1	0.47	56	6.3	7.8	21.7	31.8	2.0
G November	12.1	31.5	2.46	279	47.1	14.2	71.5		
(n=153)	2.2	16.4	0.44	41	5.3	10.7	24.6		

a Pb values below detection limit excluded

b Mean values

c Standard deviation

Table IV: Metal content, percent sand content and loss on ignition of Fraser delta-front sediments (all data on finer-than 80-mesh material).

(45%), Cu (75%) and Pb (85%), but does not apply to Ni and Mn contents. The relative total metal content of fore-slope and intertidal samples is apparent in metal distribution maps (Figs. 7 to 13). It is also apparent from these maps that intertidal sediment contents of Cu, Fe, Pb and Zn are highest nearest to shore, while the reverse is true of sediments on the fore-slope. The fore-slope region displays an even more marked trend in these elements, and to a lesser extent Co and Mn, whereby total metal concentrations increase in a northwesterly direction from the U.S. border to the mouth of the Main Arm, and then gradually increase northward along the slope of Sturgeon Bank to the vicinity of Point Grey. These trends are interrupted only by relatively lower metal values in sediments directly off the mouth of the main channel and especially the North Arm. Sediments from the northern part of the study area are therefore markedly enriched in, for example, Zn, Cu and Pb (2x, 3 to 4x and 10x higher respectively) compared with those from the southern extremity. Trends of metal enrichment are shown by representative north-south and east-west transects of Pb and Zn values in samples from the fore-slope west of Sturgeon Bank and the North Arm (Fig. 14).

This general pattern of total metal distribution appears to be inversely related to sediment grain size, as represented by the distribution of sand in surficial sediments (Fig. 15). In other words, regions of the delta-front rich in fine grained material, such as nearshore portions of the intertidal zone and the slope west of Sturgeon Bank, are the richest in metals, while regions of high sand content, such as the western part of the

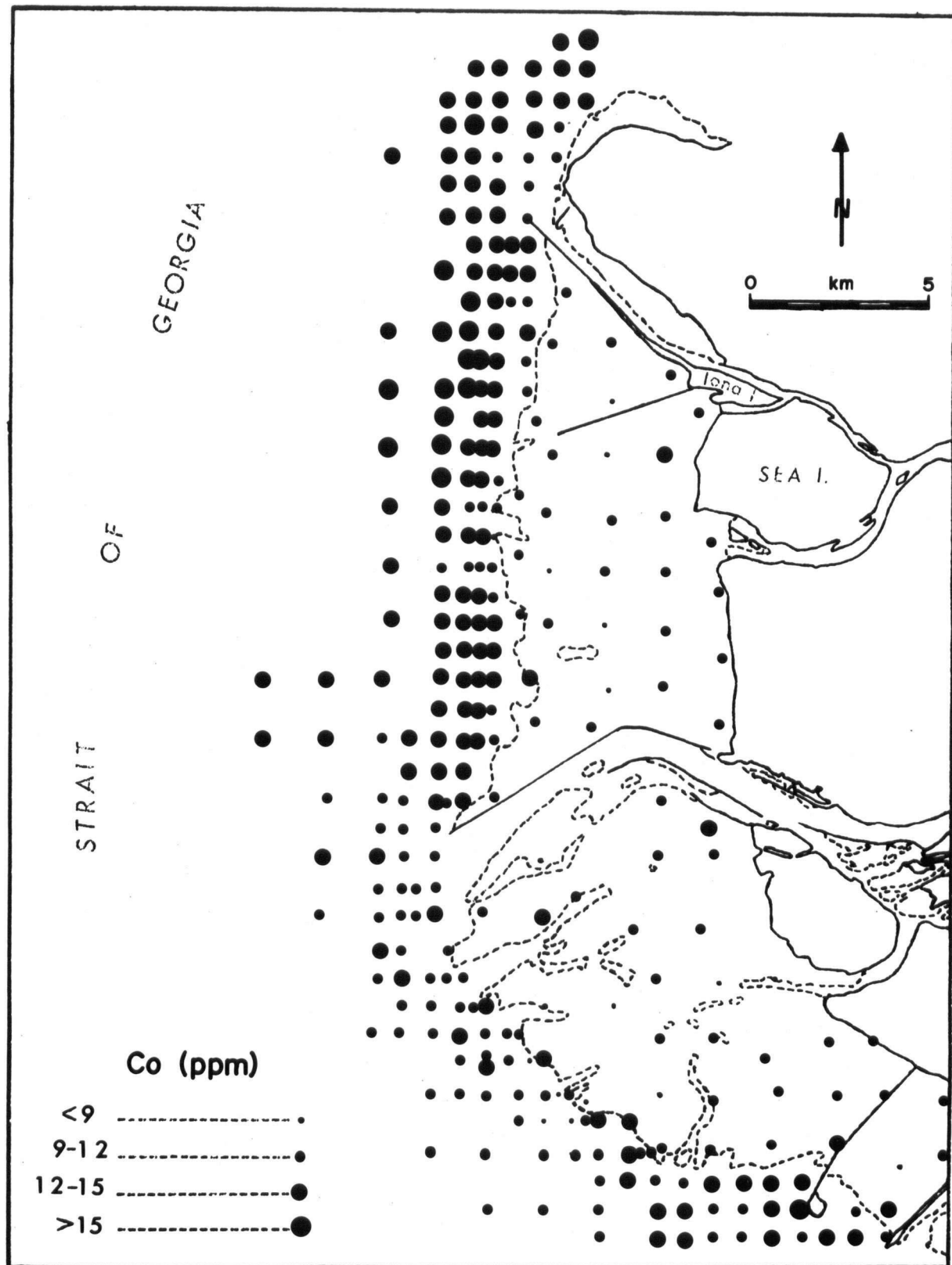


Figure 7: Distribution of Co in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

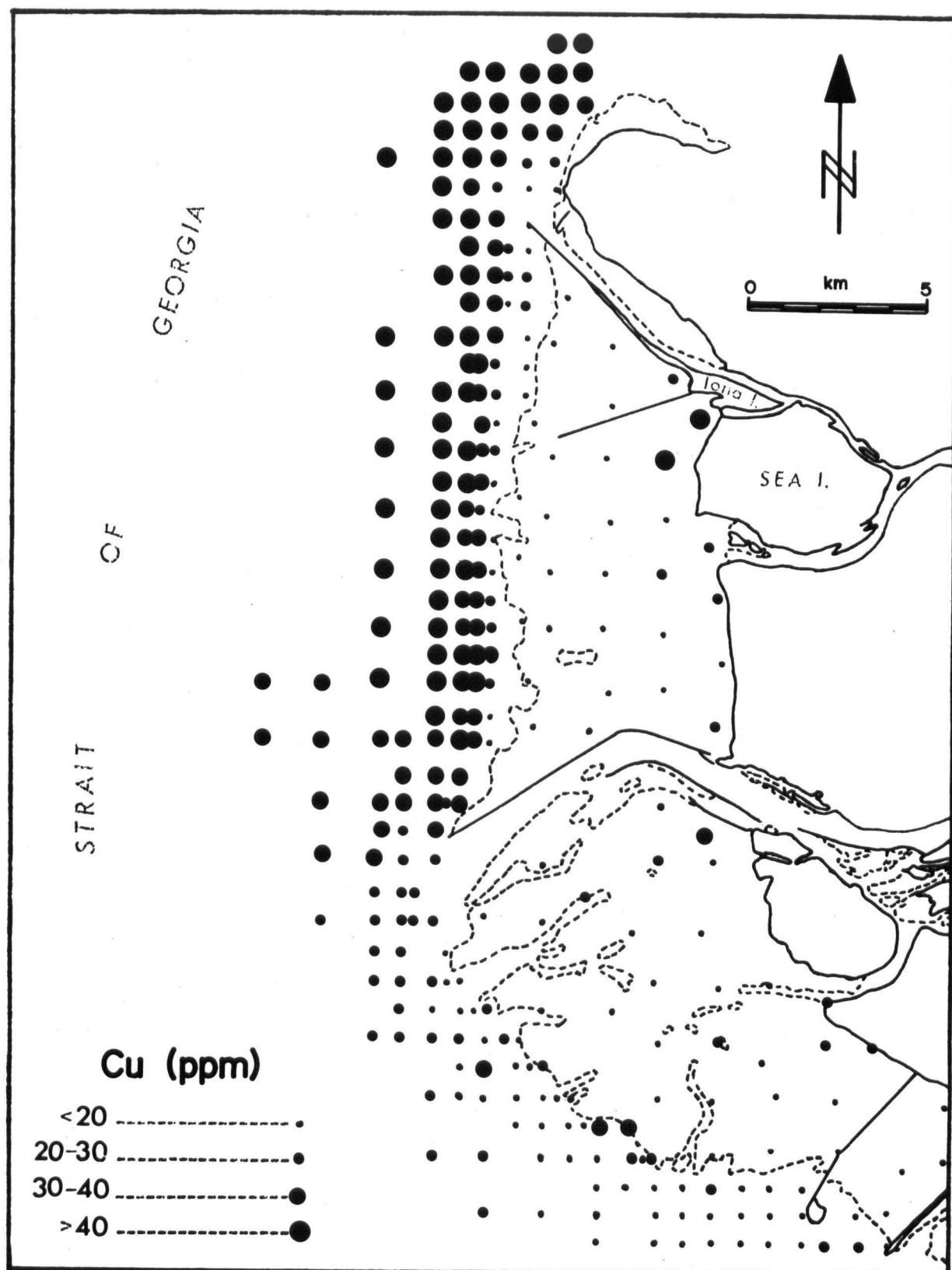


Figure 8: Distribution of Cu in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

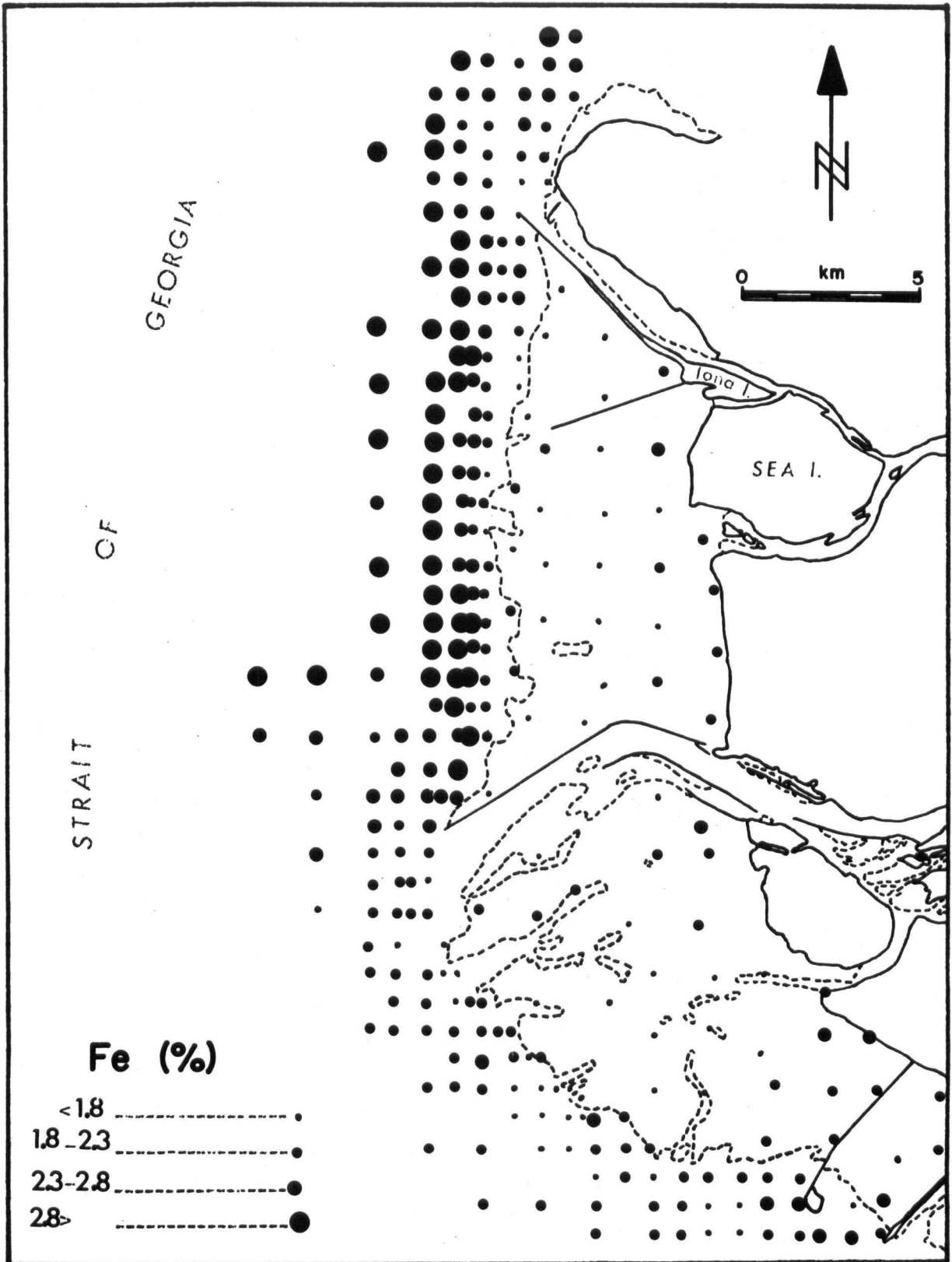


Figure 9: Distribution of Fe in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).



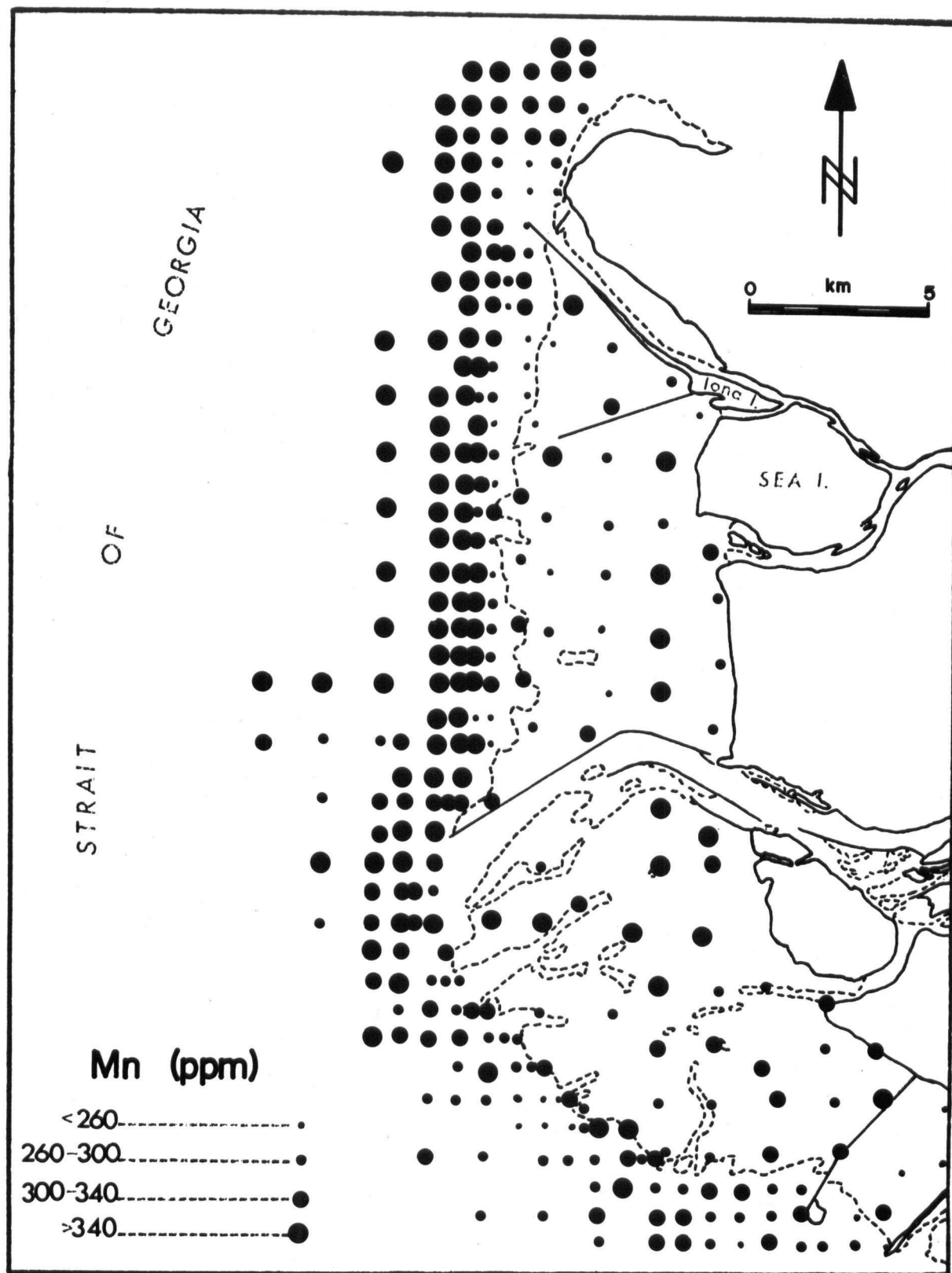


Figure 10: Distribution of Mn in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

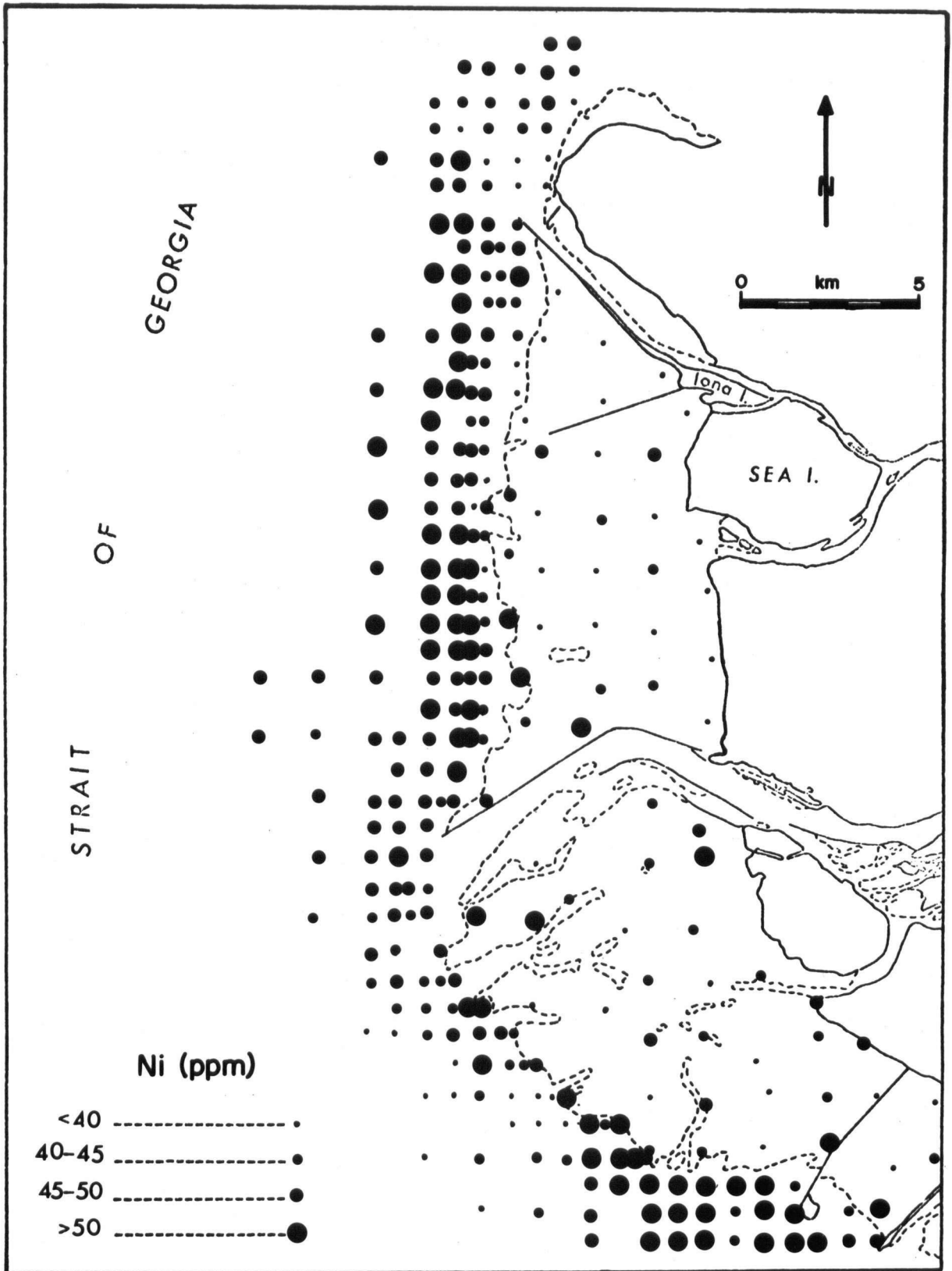


Figure 11: Distribution of Ni in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

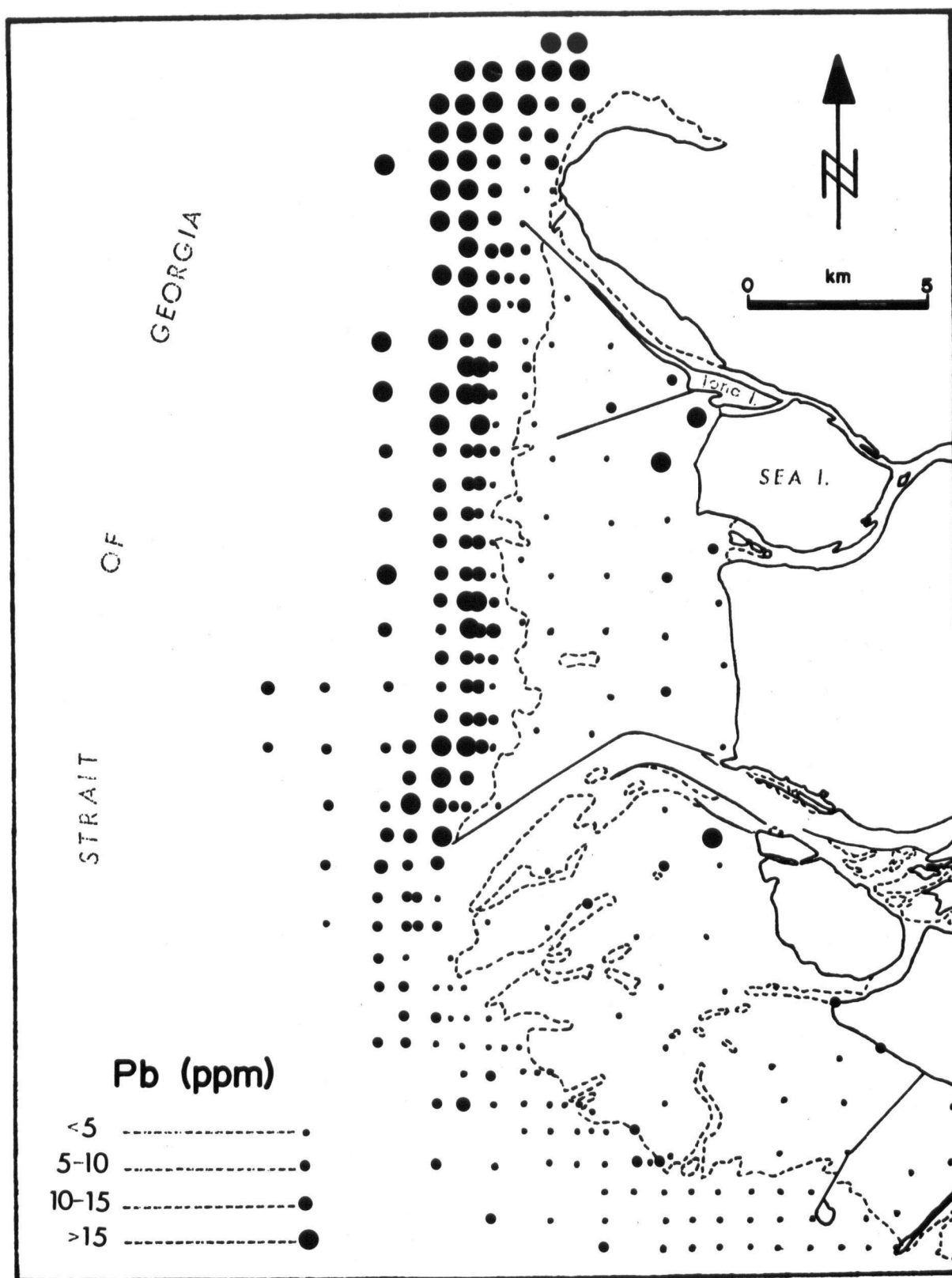


Figure 12: Distribution of Pb in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

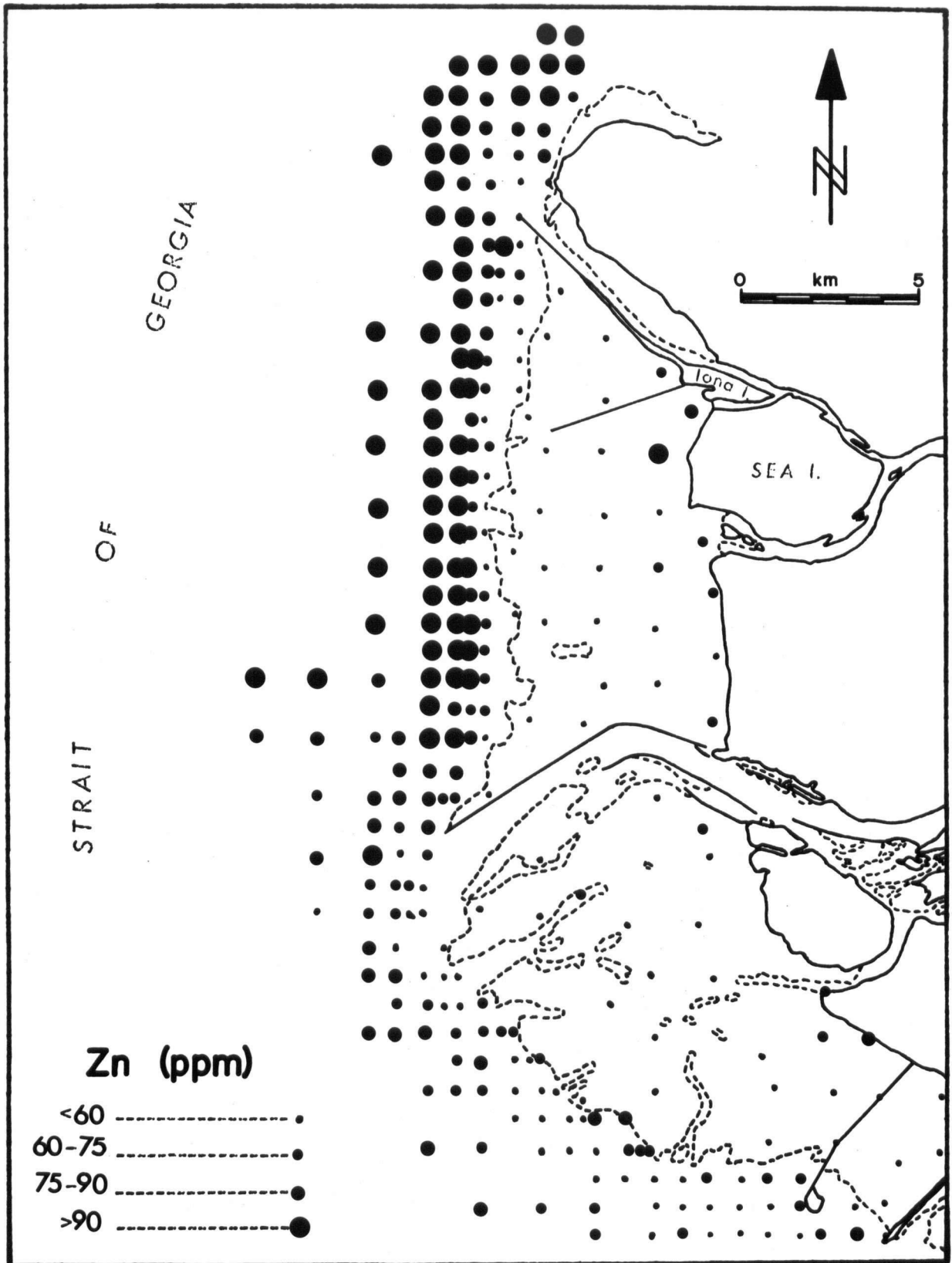


Figure 13: Distribution of Zn in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

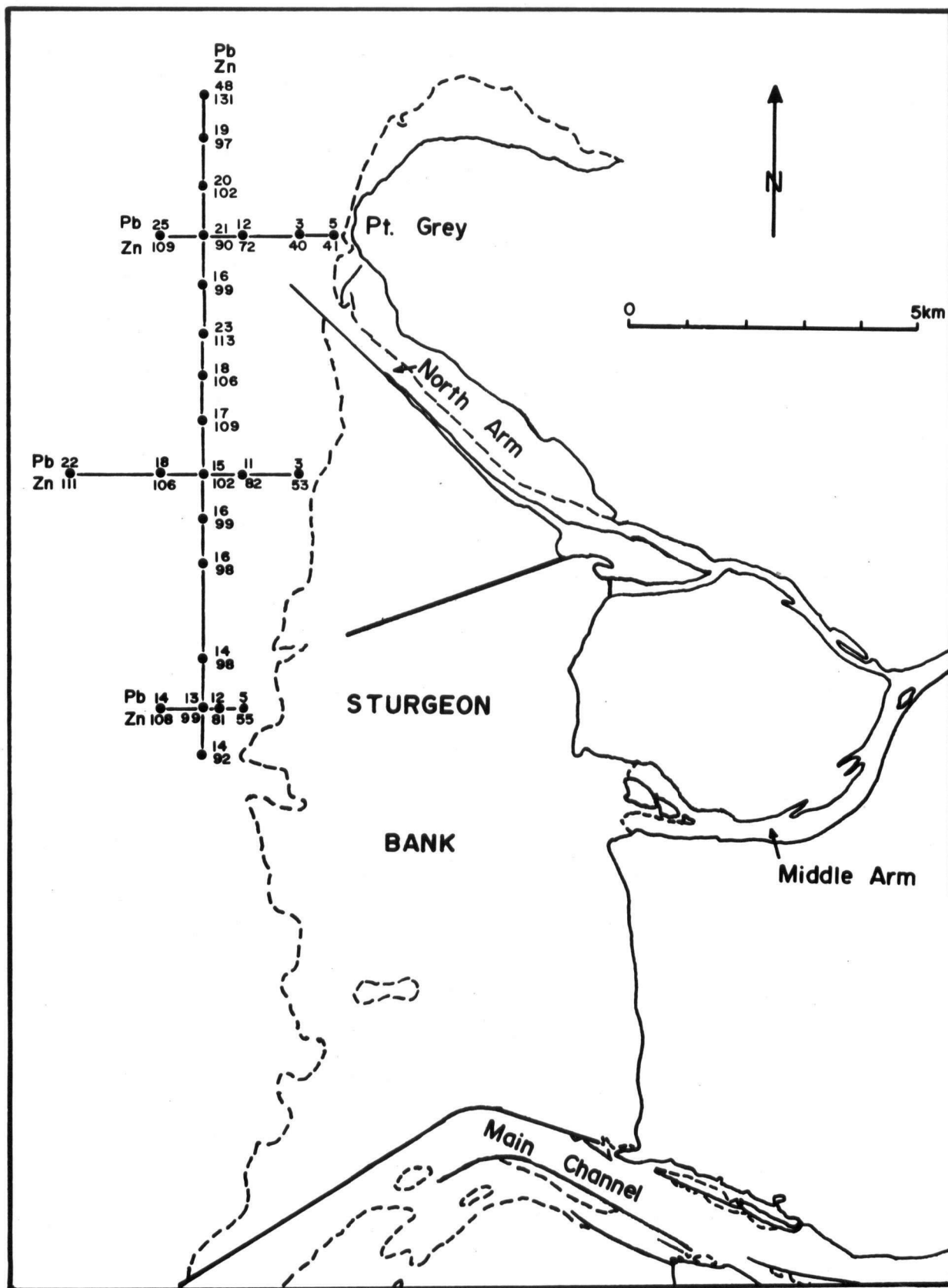


Figure 14: Pb and Zn contents (ppm) of selected surficial sediments from the fore-slope west of Sturgeon Bank (March sampling series).

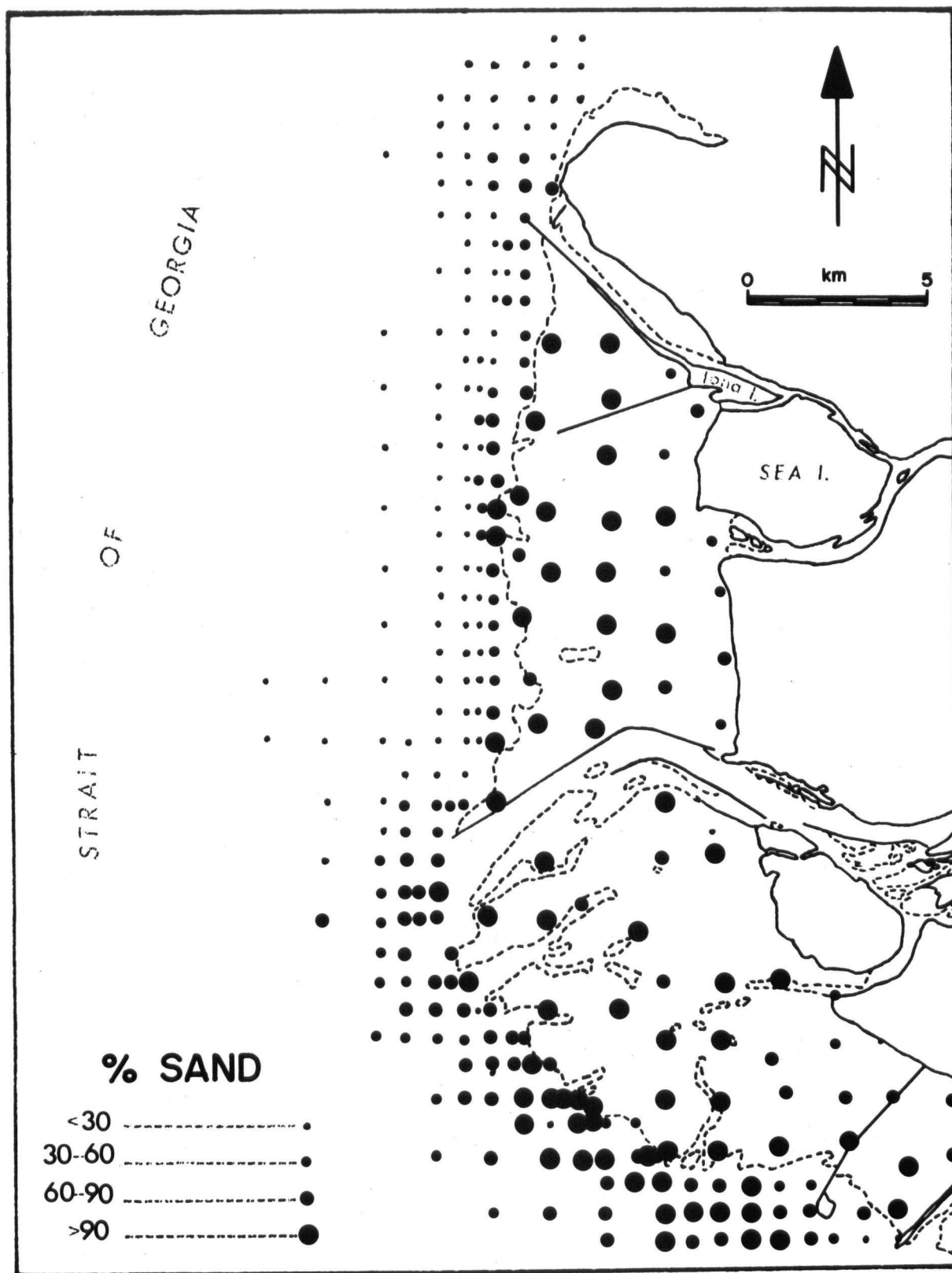


Figure 15: Distribution of sand (plus270-mesh) in the minus80-mesh fraction of Fraser delta-front surficial sediments (February and March sampling series).

tidal flats and the slope west of Roberts Bank, are the poorest. Moreover, gradual trends of metal enrichment, such as those displayed in Fig. 14, are related to decreases in sand content (Fig. 15), most noticeably in the regions west of Sturgeon Bank and the mouth of the North Arm.

Two samples collected directly southwest of Iona Island contain abnormally high concentrations of Cu (43 and 47ppm), Pb (39 and 29ppm) and Zn (83 and 95ppm) compared to intertidal sediments elsewhere (Figs. 8, 12 and 13).

### Correlation and Regression Analysis

Statistical analysis of total metal contents of delta-front sediments reveals strong positive correlations between metals with the most well defined geographic trends (Cu, Fe, Pb and Zn, and to a lesser extent, Co) and strong negative correlations between these metals and sand content (Tables V and VI). Mn is highly positively correlated with the above metals and negatively correlated with sand content on the fore-slope. Ni correlates with Co, and to a lesser extent with Fe and Mn. Loss on ignition data are negatively correlated with sand content, and positively correlated with Zn, Cu, Fe, Pb and Co in both tidal flat and fore-slope sediments, and with Mn in fore-slope sediments.

In general correlations are stronger among fore-slope sediment metal contents. Correlation coefficients between Cu, Pb and Zn contents, for example, are all above .65 in tidal flat samples, and above .85 in fore-slope samples. Negative correlations between metals and sand content are also generally stronger in fore-slope samples, as exemplified by Fe-sand correlation co-

	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>%LI</u>
<u>Cu</u>	.49							
<u>Fe</u>	.83	.59						
<u>Mn</u>	.39	.13	.26					
<u>Ni</u>	.72	.02	.53	.28				
<u>Pb</u>	.32	.72	.38	.00	.00			
<u>Zn</u>	.62	.88	.70	.10	.10	.65		
<u>%LI</u>	.36	.67	.55	-.01	-.18	.38	.72	
<u>%sand</u>	-.53	-.81	-.73	-.14	-.03	-.53	-.82	-.69

Table V: Correlation matrix for intertidal sediments collected in February, 1974 (finer than 80-mesh material; n=68; r=.24 significant at 95% confidence level).

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	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>%LI</u>
<u>Cu</u>	.69							
<u>Fe</u>	.78	.85						
<u>Mn</u>	.68	.76	.85					
<u>Ni</u>	.53	.11	.38	.43				
<u>Pb</u>	.55	.87	.68	.67	-.01			
<u>Zn</u>	.70	.93	.89	.82	.19	.85		
<u>%LI</u>	.45	.68	.66	.59	.08	.52	.70	
<u>%sand</u>	-.70	-.92	-.87	-.68	-.09	-.76	-.90	-.69

Table VI: Correlation matrix for fore-slope sediments collected in March, 1974 (finer than 80-mesh material; n=218; r=.13 significant at 95% confidence level).



efficients of  $-.73$  and  $-.87$  in tidal flat and fore-slope samples respectively.

As total trace metal contents of marine sediments are often influenced by texture, and abundance of organic matter, mafic minerals and hydrous oxides of Fe and Mn (Chester, 1965), it is reasonable to reexpress correlations as linear regression equations in which independent variables are chosen to represent these characteristics. Unfortunately none of the available data are fully independent, which places a constraint on interpretation of results. Nevertheless, independent variables chosen were %sand (to represent sediment texture), %LI (to represent organic content), total Fe (to represent mafic minerals and iron oxides) and total Mn (to represent manganese oxides). The trace metals were the dependent variables, and a stepwise multiple regression was employed (p. 35) (Bjerring and Seagraves, 1974).

Results (Tables VII and VIII) indicate that, with the exception of Pb in tidal flat samples and Ni in fore-slope samples, combinations of the independent variables account for more than 60% of variability in all dependent variables. Furthermore all dependent variables except Co are dependent on sand content. However, in the case of Ni, unlike the other trace metals, the regression equations predict that an increase in sand content will produce an increase in Ni content. Regression equations therefore generally confirm the previously observed inverse relationship between Cu, Pb and Zn values and sediment texture. The degree of dependence is demonstrated for Zn contents in fore-slope samples in Fig. 16, where normalized residuals for the regression of Zn on %sand ( $r^2 = 81\%$ ) are plotted geographically. The map suggests

<u>Dependent Variable</u>		<u>Regression</u>	<u>(r<sup>2</sup>)<sup>a</sup></u>
Co	=	2.6121 + 4.6755 Fe	68%
Cu	=	40.8860 - .2899 sand	65%
Ni	=	-23.2233 + 32.3235Fe - 3.7563 LI + .1644sand	68%
Pb	=	23.8973 - .2219sand	28%
Zn	=	71.7695 + 3.3345LI - .3068sand	72%

a  $r^2$  = percent variance accounted for by independent variables

Table VII: Multiple regression equations, intertidal sediments collected in February 1974 (finer than 80-mesh material; n=68).

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<u>Dependent Variable</u>		<u>Regression</u>	<u>(r<sup>2</sup>)<sup>a</sup></u>
Co	=	6.4548 + 2.94Fe	60%
Cu	=	29.9390 + 5.8956Fe - 0.3026sand	85%
Ni	=	-0.7848 + 16.9150Fe + 0.1990sand	38%
Pb	=	3.8429 + 0.0403Mn - 0.1377sand	62%
Zn	=	48.4373 + 0.1484Mn - 0.4362sand	88%

a  $r^2$  = percent variance accounted for by independent variables

Table VIII: Multiple regression equations, fore-slope sediments collected in March 1974 (finer than 80-mesh material; n=218).

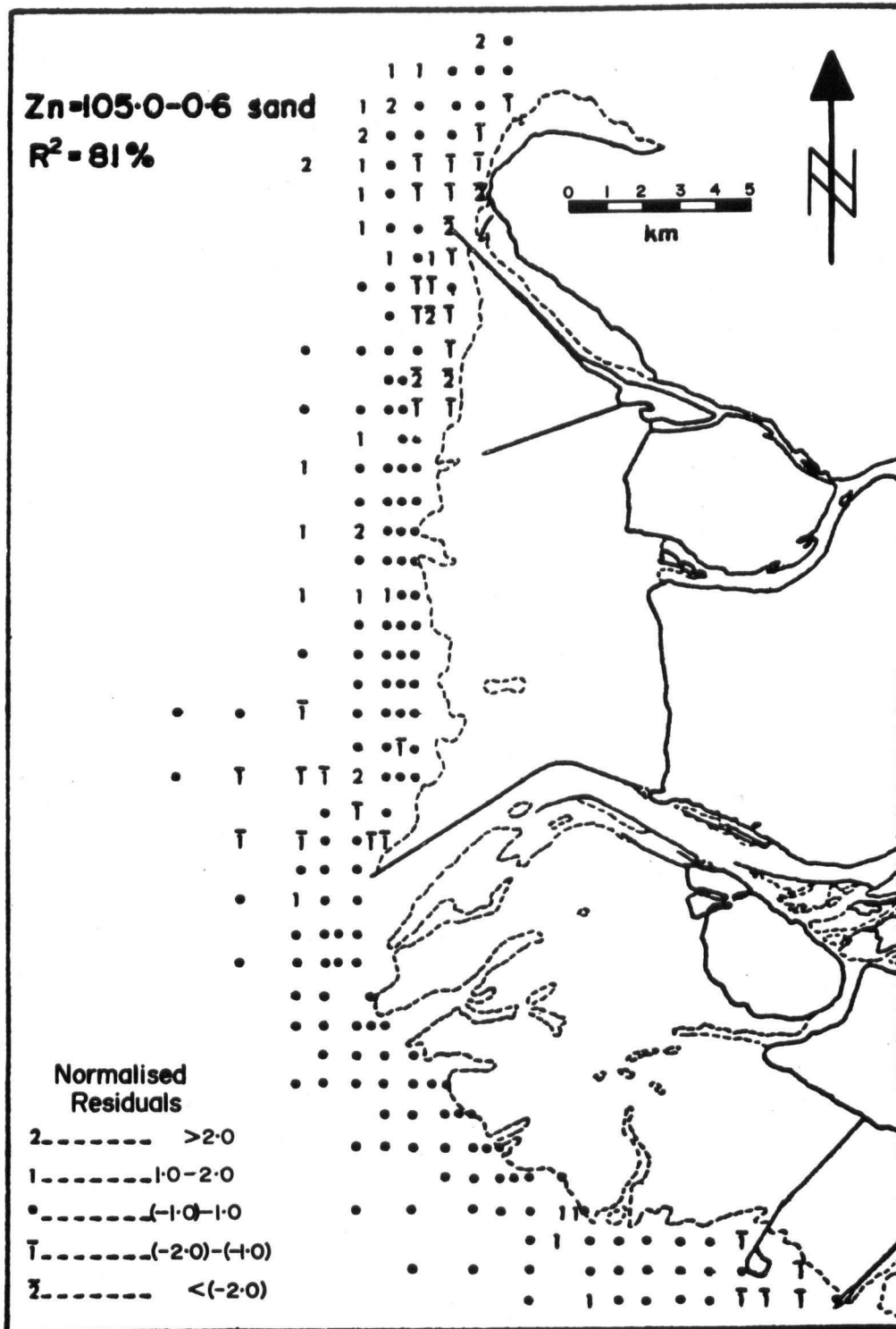


Figure 16: Distribution of normalized residuals of the regression of Zn on sand content (March sampling series).

no well defined surficial trend in Zn values is present other than that related to distribution of sediment grain size.

Most regression equations include the variables Fe and/or Mn, often in conjunction with the other independent variables, as, for example, in the combination Mn-%sand which accounts for 62% and 88% of the variability in Pb and Zn data from fore-slope sediments. Loss on ignition, together with Fe and/or %sand, contributes to regression equations of Cu, Ni and Zn in intertidal sediments and Co in fore-slope sediments.

Cu, Pb and Zn concentrations in the two metal-rich tidal flat samples southwest of Iona Island are higher than predicted by regression equations (Table IX). Normalized residuals of 2.0 and 3.0 standard deviations represent 2.5% and .5% frequency of occurrence respectively. Normalized residuals for Cu (4.5 and 3.8), Pb (3.8 and 2.2 ) and Zn (4.4 and 3.1), therefore provide evidence of the anomalous character of these samples.

#### Selective Chemical Extraction Experiments

Results of correlation and regression analysis, though difficult to interpret in terms of actual geochemical processes, do suggest the types of experiments which should be undertaken to discover the physical and chemical sediment fractions in which metals are bound. In this case negative correlations with sand content suggest some of the trace metals are perhaps absorbed on fine particles, while presence of Fe and/or Mn in regression equations suggests the possibility of metals associated with either amorphous Fe and Mn oxides or mafic minerals.

<u>Element</u>	<u>Observed Value(ppm)</u>	<u>Predicted Value(ppm)</u>	<u>Residual(ppm)</u>	<u>Normalized Residual<sup>a</sup></u>
Cu	42.6	22.6	20.0	4.5
	47.2	30.5	16.7	3.8
Pb	38.9	9.1	29.8	3.8
	29.1	12.4	16.7	2.2
Zn	83.4	58.0	25.4	4.4
	94.8	76.7	18.1	3.1

a number of standard deviations

Table IX: Observed, predicted and residual values from regression equations (Table VII) for tidal flat stations affected by discharge of metal-rich sewage effluent.

Experiments were therefore undertaken on selected intertidal and fore-slope samples using 1M  $\text{MgCl}_2$  to extract metals adsorbed onto surfaces of particles (Gibbs, 1973), and 1M hydroxylamine hydrochloride in 25% acetic acid (HHA) to dissolve and extract trace metals from amorphous Fe and Mn hydrous oxides (Chester and Hughes, 1967). Residues were taken up in strong acids to extract metals bound in detrital mineral lattices.

The first experiment involved treating minus 80-mesh material sequentially with  $\text{MgCl}_2$ , HHA and  $\text{HNO}_3\text{-HClO}_4$ . Results (Appendix B; Table X) show that, with the exception of the two anomalous samples from near Iona Island, concentrations of  $\text{MgCl}_2$ -extractable metals are small compared to hydrous oxide- and lattice-bound forms. In fact, levels of exchangeable Pb, Co and Ni are undetectable, while Cu levels are .5ppm and less, and Zn extractable in  $\text{MgCl}_2$  averages .6ppm. Fe is consistently detectable in  $\text{MgCl}_2$ -extract with a mean of 5.2ppm, although compared with total iron contents of 2 to 3%, this contribution is negligible.  $\text{MgCl}_2$ -extractable Mn on the other hand forms an average of 14.2ppm or 5% of total sediment Mn. Concentrations of Cu, Pb and Zn extracted in 1M  $\text{MgCl}_2$  from the two anomalous stations near Iona Island are strikingly high compared with levels in other tidal flat sediments (Table XI).

HHA extracts approximately 10% of the total Cu, Fe and Ni contents of sediment samples and between 15 and 20% of Zn and Co (Table X). HHA-extractable Mn averages 20% of total Mn, although the amount extracted varies from 8.8 to 134ppm. Pb is the only metal which occurs predominantly in a form soluble in

Element	<u>Extraction (ppm)</u>		
	<u>1M MgCl<sub>1</sub></u>	<u>HHA</u>	<u>HNO<sub>3</sub> - HClO<sub>4</sub></u>
Co	* *	2.6 <sup>a</sup>	11.2
		1.4 - 5.5 <sup>b</sup>	7.2 - 14.6
Cu	*	3.5	23.2
		0.8 - 6.4	7.6 - 95.8
Fe	5.6	0.24(%)	2.24(%)
	1.9 - 15.2	.11 - .41	1.66 - 3.20
Mn	14.6	60.5	202
	0.7 - 37.0	9.8 - 134	158 - 275
Ni	* *	3.8	36.7
		2.6 - 7.4	25.7 - 52.9
Pb	*	5.7	*
		0.4 - 19.7	
Zn	0.5	11.4	52.1
	<0.1 - 1.5	4.1 - 24.7	31.4 - 86.5

a mean

b range

\* not detected in most samples

\* \* not detected in all samples

Table X: Mean and range of metal values in sequential extracts of delta-front sediments (n=37).

<u>Element</u>	<u>Extraction(ppm)</u>					
	<u>1M MgCl<sub>2</sub></u>		<u>HHA</u>		<u>HNO<sub>3</sub> - HClO<sub>4</sub></u>	
Co	*	*	1.8	3.5	10.9	12.8
Cu	5.9	1.1	15.8	11.2	31.7	34.0
Fe	6.4	6.8	0.21%	0.34%	1.7%	2.4%
Mn	1.3	37.9	8.8	64.2	151	217
Ni	*	*	3.0	4.2	28.2	37.8
Pb	2.2	*	49.7	22.3	9.0	3.0
Zn	6.4	6.8	22.0	26.1	41.6	62.8

\* not detected

Table XI: Sequential extraction of tidal flat sediments from two stations affected by discharge of metal-rich sewage effluent.



HHA, and is usually not detected in the residue.

The second experiment involved leaching of silt-plus-clay and sand fractions of seven selected samples with HHA, and subsequent digestion of silt-plus-clay, light sand ( $S.G. \approx 2.89$ ) and heavy sand in  $HF-HNO_3-HClO_4$  (p. 28). As in the previous experiment all metals except Pb exist predominantly in a form insoluble in HHA (Table XII). The silt-plus-clay fraction is enriched in HHA-extractable Cu, Fe, Mn, Pb and Zn, but not Co and Ni, compared with the sand fraction, although the enrichment factor is only about 1.5 times. Silt-plus-clay contains 5 to 10% of its total Ni and Fe, 15 to 20% of total Zn, Cu and Mn, and 20 to 25% of total Co in HHA-extractable form.

A more marked contrast exists between sand and silt-plus-clay in the amount of metals extracted with  $HF-HNO_3-HClO_4$  (Table XII). The latter fraction contains 1.5 to 3 times more of all metals than the light sand fraction. Contrast between the residual metal content of the light and heavy sand fractions is even greater. Average enrichment factors in the heavy fraction are 2.3x (Cu), 3.9x (Zn), 4.8x (Ni), 6.2x (Fe), 7.0x (Co) and 9.2x (Mn). All heavy sand samples contain similar metal values, although the contribution to total values will differ since heavy sand ranges from 2 to 25% of the samples by weight.

### Discussion

Total metal contents of nearshore sediments from several localities including the Fraser delta fore-slope are listed in

Metal Contents of Extractions (ppm)

Sample and Fraction	HHA						HF-HNO <sub>3</sub> -HClO <sub>4</sub>						Sand (%)	Heavy Minerals (%)
	Co	Cu	Fe(%)	Mn	Ni	Zn	Co	Cu	Fe(%)	Mn	Ni	Zn		
A4	-270 <sup>a</sup>	4.9	5.4	.38	64.2	5.9	13.0	14.6	27.8	4.19	489	54.4	83.1	
		5.0	3.6	.26	47.1	5.2	10.4	6.2 <sup>c</sup>	13.4	1.69	201	31.0	43.5	50.0
								31.7 <sup>d</sup>	24.5	10.0	1770	116	147	5.8
A21	-270	5.4	3.2	.33	41.0	4.3	13.0	14.7	19.4	4.34	562	52.5	80.5	
		4.8	2.3	.27	39.8	3.7	12.6	3.3	11.0	1.39	186	24.7	40.3	65.8
								31.2	27.5	10.6	1940	118	160	7.8
A25	+270	6.1	3.2	.18	49.6	6.5	5.9	3.3	12.2	1.20	176	17.3	32.3	94.9
								34.8	24.5	10.8	2410	166	120	26.4
A53	-270	4.9	4.7	.31	132	2.9	15.7	15.2	25.4	4.37	599	49.7	99.7	
		6.2	4.1	.29	97.1	4.4	14.4	4.4	15.8	1.34	171	28.9	37.6	60.6
								36.6	39.5	9.51	1830	125	168	5.2
B32	-270	3.8	6.0	.40	94.7	4.4	19.3	14.8	33.8	3.79	379	45.1	88.5	
		7.4	4.1	.33	53.2	5.4	13.0	5.1	17.0	1.67	176	28.0	13.5	55.8
								31.2	36.5	9.92	1700	109	159	5.0
B119	-270	3.1	7.1	.35	75.2	5.9	17.1	13.6	35.0	3.62	445	48.9	88.2	
		3.5	5.0	.32	58.1	6.2	12.6	4.4	20.6	1.91	246	36.0	53.0	22.8
								38.0	54.5	11.2	1950	110	199	1.7
B214	-270	3.6	4.9	.37	125	6.2	17.1	12.5	38.6	3.82	445	41.1	87.6	
		5.1	3.4	.33	100	6.1	12.6	8.3	21.8	1.94	202	27.6	51.6	40.2
								38.0	54.5	11.7	1660	117	176	3.4

a silt-plus-clay

b sand

c light sand (S.G. &lt; 2.89)

d heavy sand (S.G. &lt; 2.89)

Table XII: Sequential extraction of delta-front sediments; partitioning of metals between HHA-extractable and HF-HNO<sub>3</sub>-HClO<sub>4</sub>-extractable silt-plus-clay and sand.

Table XIII. Rigorous comparisons are not possible as sediment textures and materials differ between various localities, as do degrees of industrial contamination. Moreover different sediment fractions and digestion techniques are used by various laboratories, resulting in different proportions of total metal being isolated. Despite these inconsistencies the similarity of Fraser delta-front sediments and those from other regions in terms of trace metal contents is striking. The Fraser delta-front contains relatively high values of total sediment Zn, Ni and Cu, and relatively low values of Mn when compared with most regions (q.v., Gupta and Chen, 1975; Slatt, 1974; Perkins et al, 1973; Hirst, 1962b). Polluted sediments (Severn and Clyde estuaries) contain considerably elevated values of Pb, Zn, Fe and Mn, and Co and Cu in the case of the Clyde, compared with Fraser sediments (Perkins et al, 1973; Chester and Stoner, 1975).

Geographic trends of trace metals in surficial sediments of the Fraser delta-front, and correlation and regression analyses of metal data, all indicate an inverse relationship between the metals studied (except Ni) and sand content of the sediment (Figs. 7 to 16; Tables V to VIII). In other words fine sediments and sediment fractions contain higher concentrations of Co, Cu, Fe, Mn, Pb and Zn than sands. This interpretation is corroborated by selective extraction experiments in which all metals except Co and Ni are enriched in the HHA-extractable fraction of silt-plus-clay, and all metals are enriched in the silt-plus-clay residue after HHA leaching (ignoring the heavy sand fraction).

	<u>Co</u>	<u>Cu</u>	<u>Fe(%)</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>
Fraser delta-front foreslope (sands and silts) (this study)	13	30	2.3	327	48	11	77
Los Angeles Harbour (silty sand) (Gupta and Chen, 1975)	-	35	2.9	381	18	32	94
Conception Bay (muddy sand) (Slatt, 1974)	23	25	3.2	490	51	-	50
Solway Firth (<204um fraction) (Perkins <u>et al</u> , 1973)	16	10	2.0	360	38	37	63
Boca Vagre delta (sands and silts) (Hirst, 1962 a,b)	6.5	10	2.5	375	20	14	-
Severn estuary <sup>a</sup> (<61um fraction) (Chester and Stoner, 1975)	7	38	4.5	1820	36	119	280
Clyde estuary <sup>a</sup> (silt) (Perkins <u>et al</u> , 1973)	60	225	9.4	1600	69	528	1680

a described as "polluted"

Table XIII: Mean total metal contents (ppm) of nearshore sediments.

Association of metals with fine material has often been described in nearshore sediments (q.v., Slatt, 1975; Perkins et al, 1973; Gupta and Chen, 1975), although few workers provide evidence to describe the nature of this association. Trace metals in marine sediments are known to occur in various forms, including: i) incorporated in living and decayed organic material; ii) adsorbed on surfaces of clay-size and colloidal particles of clays, organic material and amorphous hydrous iron and manganese oxides; iii) bound in hydrous iron and manganese oxides of weathering, fluvial and marine origin; and iv) as constituent cations in lattices of detrital minerals (Chester, 1965; Krauskopf, 1956; Gupta and Chen, 1975; Chester and Stoner, 1975; Cooper and Harris, 1974; Nissembaum and Swaine, 1976). The sequential extraction procedures used in this study were designed to isolate metals associated with forms ii), iii) and iv). Organically bound metals were not analysed because organic matter content of delta-front sediments is low (Appendix A), and because statistical analysis indicates fewer correlations and dependencies between trace metals and %LI than between trace metals and %sand, Fe and Mn.

Abundance of surface-sorbed metals has commonly been inferred from inverse metal-grain size relations (q.v., Slatt, 1974). In the case of the Fraser delta-front low  $\text{MgCl}_2$ -soluble metal values (except Mn) militate against this interpretation. The generally sandy and silty nature of intertidal and fore-slope sediments probably accounts for the small contribution of an adsorbed metal fraction. Low and non-detectable concentrations

of adsorbed Cu, Pb, Ni and Zn are similar to results of Gupta and Chen (1975) for silty sediments from Los Angeles Harbour. Adsorbed Mn in Fraser delta-front sediments is one order of magnitude higher than in Los Angeles Harbour sediments, whereas adsorbed Fe is one order of magnitude lower, despite similar total Mn and Fe contents (Table XIII). High exchangeable Mn values are reported for sediments of the Hudson estuary (McCrone, 1967), but are related there to increased solubility of Mn in reducing conditions.

Association of almost all Pb and 10 to 20% of other metals with material soluble in HHA partially accounts for association of metals with fine sediment. Further, results suggest that large proportions of trace metals are bound in amorphous Fe and Mn hydrous oxides (Chester and Hughes, 1967). These oxides are ubiquitous in surface sediments in contact with oxygenated waters. They form, both as coatings on particules and as free colloids, in soil (Jenne, 1968), stream (Foster and Hunt, 1975), estuarine (Lowman et al, 1966) and oceanic environments (Goldberg, 1954). Their capacity to scavenge metal ions, both as adsorbed and coprecipitated species, is well known (Lee, 1975; Jenne, 1968; Krauskopf, 1956; Kharkar et al, 1968) and accounts for high trace metal levels in, for example, soil particle coatings and marine ferromanganese nodules.

Metals associated with hydrous oxides can be compared with those associated with the "nodular hydrogenous fraction" of Los Angeles Harbour sediments (Gupta and Chen, 1975) and the HHA-leachable fraction of polluted Severn Estuary sediments (Chester and Stoner, 1975) (Table XIV). Pb proportions in Fraser

	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>
Fraser delta-front <53um Metals extractable in HHA <sup>a</sup> (this study)	23	15	8	15 <sup>b</sup>	9	<100 <sup>c</sup>	16
Severn estuary <61um Metals extractable in HHA <sup>a</sup> (Chester and Stoner, 1975)	33	43	54	80	33	68	68
Los Angeles Harbour sediment <sup>d</sup> Metals extractable in NH <sub>2</sub> OH·HCl in HNO <sub>3</sub> and in HHA at 100°C (Gupta <sup>3</sup> and Chen, 1975)	-	10	12	12	22	48	29

a average values

b contains a significant proportion of adsorbed Mn

c Pb not detected in HHA residues

d sandy silt sample; 48% > 50um

Table XIV: Proportion of metals (%) in hydrous oxide phases of nearshore sediments.

	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>
Fraser delta-front <53um <sup>a</sup> (this study)	77	75	92	75	91	*	74
Severn estuary <61um <sup>a</sup> (Chester and Stoner, 1975)	67	57	46	20	67	32	32
Los Angeles Harbour sediment <sup>b</sup> (Gupta and Chen, 1975)		88	77	75	63	35	37

a average values

b sandy silt sample; 48% > 50um

\* all values below detection limit

Table XV: Proportion of metals (%) in detrital minerals of nearshore sediments.

delta-front sediments are much higher than those from the other localities, whereas fractions of Ni and Zn are lower. In all three localities the relative order of enrichment  $Pb > Zn > Cu$  is obeyed.

Trace metals bound in hydrous Fe and Mn oxides in Fraser delta-front sediments possibly represent metals scavenged in weathering environments of the Fraser drainage basin. A further contribution of Zn and Cu and probably other metals to the HHA-soluble fraction is formed on suspended sediments within the main channel between Steveston and Sand Heads (Chapter VI).

The largest proportion of Co, Cu, Fe, Mn, Ni and Zn is associated with the HHA-residue (Tables X and XII) and thus represents metals bound in crystalline minerals of detrital origin. The fine fractions are again enriched in this form of metal, although heavy minerals in the sand fraction partially counteract this relationship. Minerals in the silt-plus-clay fraction wherein trace metals can substitute for magnesium and ferrous iron in lattice sites include amphiboles, micas and chlorites. Heavy sand iron-bearing minerals include amphiboles, epidote, biotite and magnetite.

Proportions of lattice-bound iron and trace metals are greatest in nearshore sediments (Chester and Messiha-Hanna, 1970), since accumulation of terrigenous sediment is greatest in nearshore regions. Importance of this association has been demonstrated in the Severn estuary (Chester and Stoner, 1975), Los Angeles Harbour (Gupta and Chen, 1975) (Table XV) and the Gulf of Paria (Hirst, 1962a,b).

Content and distribution of total metals in Fraser delta-front sediments are therefore determined primarily by relative



abundances of silt-plus-clay, light sand and heavy sand. In other words the controlling factors are sediment transportation and sorting mechanisms which determine sediment texture. For example, accumulation of fine-grained material in salt marshes and on the fore-slope west of Sturgeon Bank results in high total metal contents because of the general enrichment of fine material in hydrous oxide- and lattice-bound metals. Introduction of metal-poor sand will produce lower total metal concentrations in a sediment, as in the region immediately west of the mouth of the North Arm. In local conditions of active winnowing by currents, as on the sand flats, and/or net removal of sediment, as on the fore-slope west of Roberts Bank, relative accumulation of metal-rich heavy minerals may partially counteract the dilutant effect of sand. Sporadic high values of metals such as Mn, Fe, Ni and Co, which are most enriched in heavy sand, will result.

Each metal is affected to a different degree by these processes, depending upon, among other factors, proportion of total metal in the HHA-soluble fraction, and proportions of HHA- and acid-extractable metal in silt-plus-clay and sand. While the overall balance is very complex (and undoubtedly involves more factors than those discussed here), the predominant effect of sediment texture can be demonstrated in the cases of two extremes:

- i) For zinc, a metal which occurs in greatest concentration in HHA- and acid-extractable silt-plus-clay (Table XII), and whose enrichment in heavy sand is relatively low, a clear inverse geographic relation exists between total zinc and sand content of sediments (Figs. 13 and 15). This is reflected in

statistical analyses (Tables V to VIII) which show strong negative correlations between total Zn and sand content and a strong dependence of Zn on sand content.

- ii) Nickel is not enriched in silt-plus-clay in the HHA-extractable fraction (Table XII). Furthermore it is relatively concentrated in heavy sand. Consequently geographic distribution appears random and no relation to grain size distribution is apparent (Fig. 11). Nonsignificant correlations with sand content thus result from association with both silt-plus-clay and sand to approximately equivalent extents.

Lead, being present predominantly in HHA-extractable form and predominantly in silt-plus-clay, displays well-defined geographic trends and strong textural correlations similar to zinc (Tables V and VI; Figs. 12 and 13). Other metals show behaviour intermediate between zinc and nickel, dependent upon factors discussed above.

In the vicinity of Iona Island the above natural mechanisms are overshadowed by discharge from the Greater Vancouver Regional District primary sewage treatment plant. Two sampling stations are defined as anomalous in total Cu, Pb and Zn contents on the basis of regression analysis (Table IX). These two samples are further distinguished by concentrations of  $\text{MgCl}_2$ -extractable Cu, Pb and Zn which are an order of magnitude higher than other delta-front samples, and levels of HHA-extractable metals which are also noticeably high (Table XI).

Hall et al (1975) report high dissolved levels of Cu (105ug/l), Zn (108ug/l) and Pb (39ug/l) in wastewater entering the Iona Island sewage treatment plant. The fate of metals in effluent from this plant is impossible to delineate on the basis of low density sediment sampling. Galloway (in Rohatgi and Chen, 1975) estimated that less than 15% of sewage-transported metal is accounted for in sediments adjacent to southern California outfalls. Rohatgi and Chen (1975) attribute this loss of metal to mixing and dilution of dissolved metals with sea water, and mobilization of metals associated with sewage particulates. This interpretation may be valid as tidal action at the Fraser delta-front allows for rapid mixing of waste and marine waters. Furthermore, presence of  $MgCl_2$ -extractable contaminant metals in sediments receiving Iona Island effluent particles suggests that considerable quantities of waste particulate metal are easily exchanged and mobilized by cations in sea water.

No doubt the organic fraction of sewage effluent is also important in transportation of metals. Particulate organic matter and associated metals may be deposited near the outfall, as observed in sediments adjacent to Los Angeles County sewage outfalls (Bruland et al, 1975). Soluble organic matter in treated sewage may also affect metal pathways by complexing metals, thus influencing their solubilities, and sorption and mobilization properties (Murray and Meinke, 1974; Theis and Singer, 1974; Rashid and Leonard, 1973).

In summary, trace metals in surficial sediments are predominantly bound in lattices of detrital minerals. Relative

enrichment of most metals in the HHA-extractable and  $\text{HNO}_3\text{-HClO}_4$ -extractable fractions of silt-plus-clay compared with sand, and enrichment of all metals studied in heavy sand minerals, accounts for total contents of metals in surficial sediments. Physical sediment transportation and deposition mechanisms determine distribution of metals on the Fraser delta-front.

CHAPTER V: TRACE METALS IN BURIED INTERTIDAL  
SEDIMENTS OF THE FRASER RIVER DELTA-FRONT

Introduction

To determine if surficial metal values are continued at depth in sediments, a series of short cores was collected from intertidal regions of the Fraser delta-front (Fig. 5). Factors expected to produce variable metal profiles include textural variations, post-depositional chemical changes, and changes in rate of metal input resulting from natural or man-made causes.

Results

Metal contents of 5cm subsamples of short cores collected at locations shown in Fig. 5 are listed in Appendix C. Selected cores are shown in Fig. 17; average metal values of cores relevant to following discussions are listed in Table XVI.

The most striking feature of short core data is the general uniformity of metal values throughout the depths sampled, particularly in cores of uniform texture (e.g., cores 16, 18, 31 and 34) (Fig. 17; Plate 1). Secondly, variations between core averages tend to be of the same order as variations between surface metal levels over the intertidal area. This is demonstrated by comparing average Zn values in core 34 (68ppm), a fine-grained salt marsh sample, and core 18 (38ppm), a coarse-grained

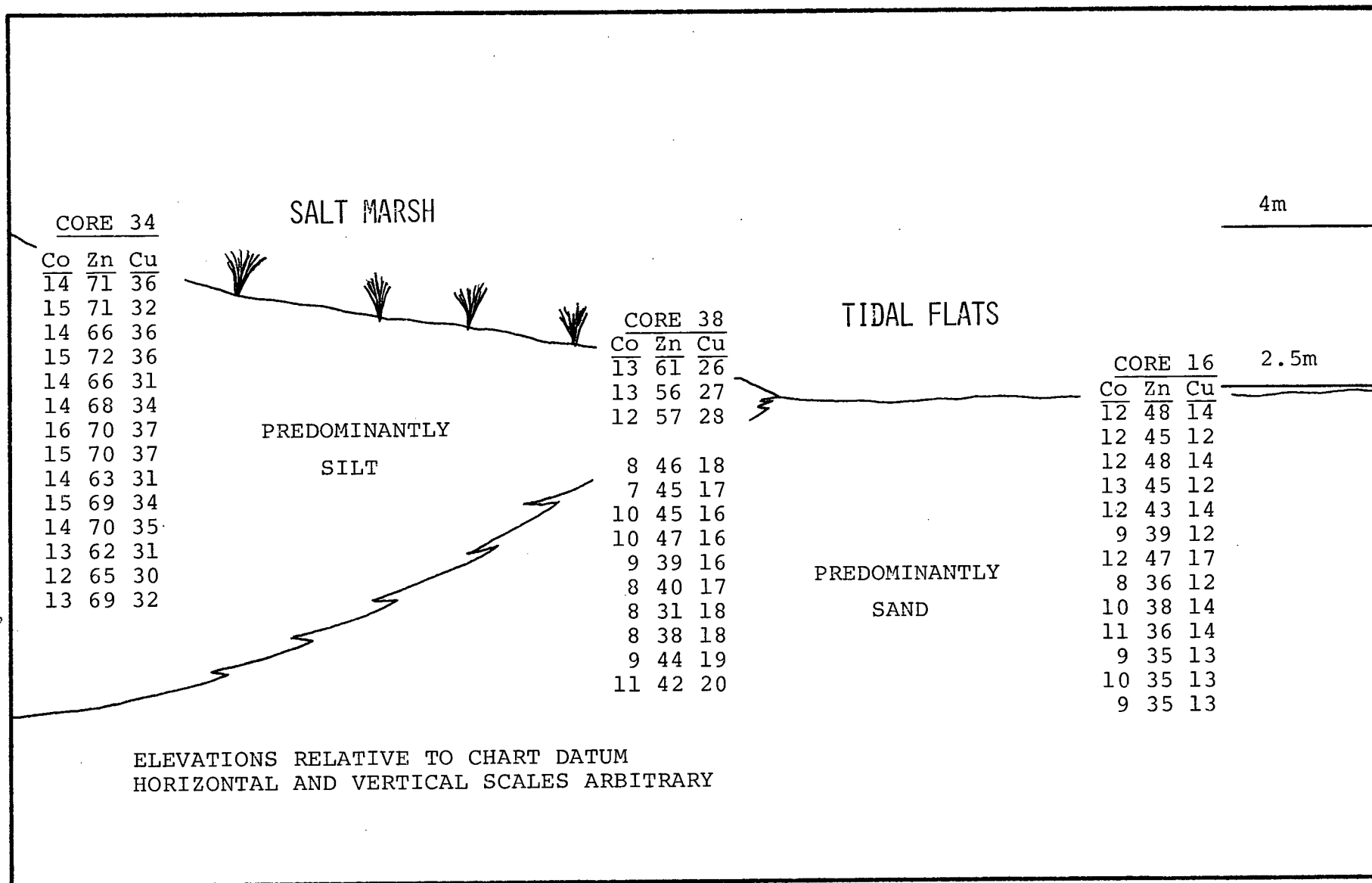


Figure 17: Schematic section of Co, Zn and Cu values (ppm) in 5cm-subsamples of subsurface sediments from Roberts Bank.

tidal flat sample, with the surficial range in Zn concentrations in February intertidal samples (38 to 79ppm). Between these two extremes, a core from the fluctuating environment near the seaward edge of the marsh (e.g., core 37) contains intermediate mean Zn values (59ppm).

This comparison suggests trace metal concentrations at depth largely depend on texture, and perhaps other sediment properties, to a degree similar to surficial sediments. It is expected, therefore, that a core with variable texture should contain variable metal concentrations. Core 38, for example, contains tidal flat sediments overlain by sediments typical of the leading edge of the salt marsh (Plate 1), resulting in an average Zn content increase from 42.8 to 61.4ppm, values typical of uniform cores from these two environments (Fig. 17). All metals except Ni are similarly affected (Fig. 17; Appendix C). Cores 19 and 35 also display abrupt shifts in mean metal contents resulting from rapid facies fluctuations (Appendix C). Gradual fluctuation of metal profiles are due to more subtle grain size fluctuations, as in core 33. Here values of Zn, for example, increase from 60 to 75ppm over a range of 70cm, in which interval the sand population becomes less dominant (Appendix C).

A very pronounced facies change from an organic-rich mud to fine sand occurs at 12cm depth in core 30, collected adjacent to the Iona Island sewage effluent outfall channel, within 1km of the point of discharge (Fig. 5). The surficial mud, which represents deposition since the blocking of MacDonald channel in combination with sedimentation of fine particulates from sewage discharge since 1963, contains levels of Cu, Pb and Zn (43, 29

		<u>Average Metal Contents(ppm)</u>							
<u>Location</u>	<u>Core</u>	<u>Co</u>	<u>Cu</u>	<u>Fe(%)</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>%sand</u>
Tidal Flats	16	10.6	13.4	1.99	234	44.4	*	40.8	95.4
	18	9.3	15.6	1.84	240	38.3	*	38.0	
	29 <sup>a</sup>	10.6	14.8	1.74	179	38.2	*	43.0	92.5
Varying conditions	33	11.7	27.7	2.36	234	43.2	6.8	63.1	53.5
	19	10.2 <sup>b</sup>	23.3	2.14	265	39.6	*	48.5	75.4
		8.8 <sup>c</sup>	15.4	1.89	265	37.5	*	38.2	96.0
	35	12.0	27.3	2.42	278	42.5	11.0	64.5	
		10.3	18.4	2.08	232	38.1	*	46.2	
	37	12.8	28.6	2.55	325	45.9	*	59.6	
Salt marsh	38	13.1	30.1	2.73	348	46.0	5.1	61.4	
		8.9	17.4	2.15	257	40.7	*	42.8	
	31	12.1	33.5	2.55	306	57.8	*	65.0	43.2
	34	14.2	33.9	2.67	269	45.9	6.6	68.2	26.0

\* some or all values below detection limit

a excluding 21-31cm depth portion

b upper fine-grained portion

c lower coarse-grained portion

Table XVI: Average metal content and sand content of intertidal sediment cores.



and 88ppm respectively) similar to contaminated surface samples from this region (Table IX).

By comparing average metal values for cores of uniform texture with values predicted by the regression equations computed for surficial samples (Table XVII), it may be possible to detect changes in metal concentration brought about by post-depositional processes or change of metal input rate to the delta-front. The mean for Cu in a tidal flat core (16), for example, is 13.4ppm, compared with a value of 13.2ppm predicted by regression based on its sand content. Cu content in two salt marsh cores (33 and 34) predicted by regression (25.5 and 33.6ppm respectively) are also very close to actual mean values of 27.7 and 33.9ppm. Core 31, with 33.5ppm Cu, contains 5ppm more than predicted. Zn and Co means in short cores, on the other hand, are roughly 10% lower than predicted values, while Ni means are 10 to 20% lower (Table XVII). The Fe values are 10 to 15% higher than predicted by a regression equation based on sand content. Mean values of Pb in cores 33 and 34 are 45% and 60% lower respectively than predicted values. However, since  $r^2=28\%$  in the case of Pb regression on sand this result should not be considered reliable. A similar comparison of Mn values cannot be made as Mn does not correlate significantly with sand content in tidal flat sediments.

### Discussion

General uniformity of metal profiles in short cores, other than those containing facies changes and obvious textural

<u>Core</u>	<u>Element</u>	<u>Actual content(ppm)</u>	<u>Predicted value<sup>a</sup>(ppm)</u>	<u>Residual(ppm)</u>
16	Co	10.6	11.9	-1.3
	Cu	13.4	13.2	+0.2
	Fe	1.99(%)	1.73(%)	+0.26(%)
	Ni	44.4	51.4	-7.0
	Pb	*		
	Zn	40.8	47.0	-6.2
31	Co	12.1	14.5	-2.4
	Cu	33.5	28.5	+5.0
	Fe	2.55(%)	2.22(%)	+0.33(%)
	Ni	51.8	58.4	-6.6
	Pb	*		
	Zn	65.0	69.1	-4.1
33	Co	11.7	13.6	-1.9
	Cu	27.7	25.5	+2.2
	Fe	2.36(%)	2.12(%)	+0.24(%)
	Ni	43.2	55.3	-12.1
	Pb	6.6	12.0	-5.4
	Zn	63.1	64.7	-1.6
34	Co	14.2	15.1	-0.9
	Cu	33.6	33.9	+0.3
	Fe	2.67(%)	2.37(%)	+0.30(%)
	Ni	45.3	58.2	-12.9
	Pb	6.8	18.1	-11.3
	Zn	68.2	76.4	-8.2

\* some or all values below detection limit

a Regressions:

$$\begin{aligned}
 \text{Co} &= 2.6121 + 4.6755(\text{Fe}) & r^2 &= 68\% \\
 \text{Cu} &= 41.2767 - .2947 (\% \text{ sand}) & r^2 &= 65\% \\
 \text{Fe} &= 6.2186 - .009337 (\% \text{ sand}) & r^2 &= 54\% \\
 \text{Ni} &= -23.3637 + 32.3235(\text{Fe}) & & \\
 &\quad -3.7909(\% \text{ LI}) + .1689(\% \text{ sand}) & r^2 &= 67\% \\
 \text{Pb} &= 23.8973 - .2219(\% \text{ sand}) & r^2 &= 28\% \\
 \text{Zn} &= 87.3560 - .4428(\% \text{ Sand}) & r^2 &= 67\%
 \end{aligned}$$

Table XVII: Predicted and residual values of average metal contents in intertidal sediment cores; regression equations taken from data for February tidal flat samples.

variations, and similar ranges of total metal contents in core and surface samples over the intertidal region, are related to the preponderance of trace metals associated with detrital minerals in this area (Chapter IV). In other words the bulk of deposited metals (excepting Pb) is unavailable for chemical reactions under early diagenetic conditions. However, apparent losses of Pb, Zn, Co and Ni from buried sediments (Table XVII) suggests, assuming metal input has been constant with time, some post-depositional mobilization of these metals. The fractions of metal affected are uncertain without further analysis, but they are most likely the adsorbed and hydrous oxide-associated fractions. In support, the apparent losses of Zn, Co and Ni are similar to HHA-extractable proportions of total metal (Tables X and XII), and Pb, the metal most enriched in HHA-extract, exhibits by far the largest apparent loss. Duchart et al (1973) have suggested that Fe and Mn oxides are solubilized at depth in sediments as a result of decreasing Eh, with consequent release of sorbed and coprecipitated trace metals. Once mobilized in this manner into interstitial waters, organic complexing may maintain metals in soluble form (Presley et al, 1972; Elderfield and Hepworth, 1975; Duinker et al, 1974). Metals may subsequently be transported to the sediment surface by diffusion (Elderfield and Hepworth, 1975) particularly in areas experiencing high current velocities (Duinker et al, 1974).

Militating against this interpretation are several factors, including the lack of direct analytical evidence of metal forms and Eh conditions at depth. Further, Cu and Fe are apparently not mobilized, yet are known to occur in hydrous oxides to

the same extent as other metals. The behaviour of Fe data in particular suggests either the presence or nature of the mobilization process is indefinite. Finally, the assumption that metal input to the delta-front has been constant over the time represented by the cores, must be suspect. At least in the Iona discharge area (Core 30) there is definite evidence of the relatively recent introduction of metal-rich contaminated organic-rich muds. Contaminated levels of trace metals in bottom sediments of the lower Fraser (Hall and Fletcher, 1974) would lead one to expect higher concentrations of metals in sediments reaching the entire delta-front today.

The problem of post-burial metal mobilization will be resolved by partial extraction of metals in subsurface samples, and analysis of interstitial waters. Detection of changing metal input rates will be difficult, especially if diagenetic factors are influencing subsurface metal concentrations. Collection of longer cores in areas of continuous undisturbed sedimentation would be helpful, in case a marked transition exists at depths greater than those sampled in this study.

## CHAPTER VI: INTERACTIONS BETWEEN SUSPENDED SEDIMENT AND TRACE METALS IN THE MAIN CHANNEL OF THE FRASER RIVER

### Introduction

Rivers carry both dissolved and sediment-bound metal, constituting the greatest proportion of metal input to the oceans (Gibbs, 1973; Turekian, 1971). However, few detailed studies have been carried out to determine amount and mode of metal transport in rivers, and fewer still describe processes occurring in the transition from fresh to saline conditions. Estuaries, where effects of various degrees of interaction between river and marine materials can be observed, are the sites where these transitions occur.

Suspended sediment-metal interactions have been investigated to discern changes in metal association within estuarine portions of the Fraser River, and to determine if metal contents within surficial sediments of the delta-front (Chapter IV) reflect processes occurring after encounter of brackish or marine conditions. In the light of other studies (e.g., Burrell, 1973; Thomas, 1975; Lowman, 1966; de Groot, 1973), this investigation was designed to detect sorption and desorption processes involving particulate and dissolved metals. Sampling was carried out on August 19, 20 and 21, 1975, when the Fraser River discharge at Agassiz was  $2830\text{m}^3/\text{sec}$ .

## Results

Locations of 1m-depth sampling stations within the main channel are shown in Fig. 18, along with conductivities of water and relation of sampling times to tidal cycles. Tides were delayed moving upriver, up to a total of three hours at Station 9. Stations 2 through 5 were purposefully sampled near high tides to coincide with penetration of the salt water intrusion. Samples were collected at depth in saline water at stations 3, 4 and 5.

Suspended sediment levels at 1m depth decrease steadily from 25mg/l at station 9 to 4mg/l at station 2, except for the increase observed between stations 8 and 7 (Fig. 19). Only a small change was found between stations 5 and 4. Total particulate major elements (Ca, Mg, Na and K) per weight of particulates are roughly constant, and thus values of these elements per volume of water parallel the decrease in suspended sediments moving downriver (Table XVIII).

Data of total and HHA-extractable suspended Zn ( $Zn_s$  and  $Zn_e$ ), Fe ( $Fe_s$  and  $Fe_e$ ) and Mn ( $Mn_s$  and  $Mn_e$ ), total suspended Cu ( $Cu_s$ ), and dissolved Zn ( $Zn_d$ ), Cu ( $Cu_d$ ) and Fe ( $Fe_d$ ) are displayed in Fig. 19 and Table XIX. Changes in concentration of total suspended Fe and Mn closely follow variations in suspended sediment load, similarly to the major cations. Suspended Zn follows the same trend in the fresh water between stations 9 and 5. However, in the brackish waters between stations 5 and 4 there is an increase from 2.8ug/l to 5.8ug/l, equivalent to a change of 167ppm to 349ppm dryweight of sediment. Concentrations of dissolved Zn

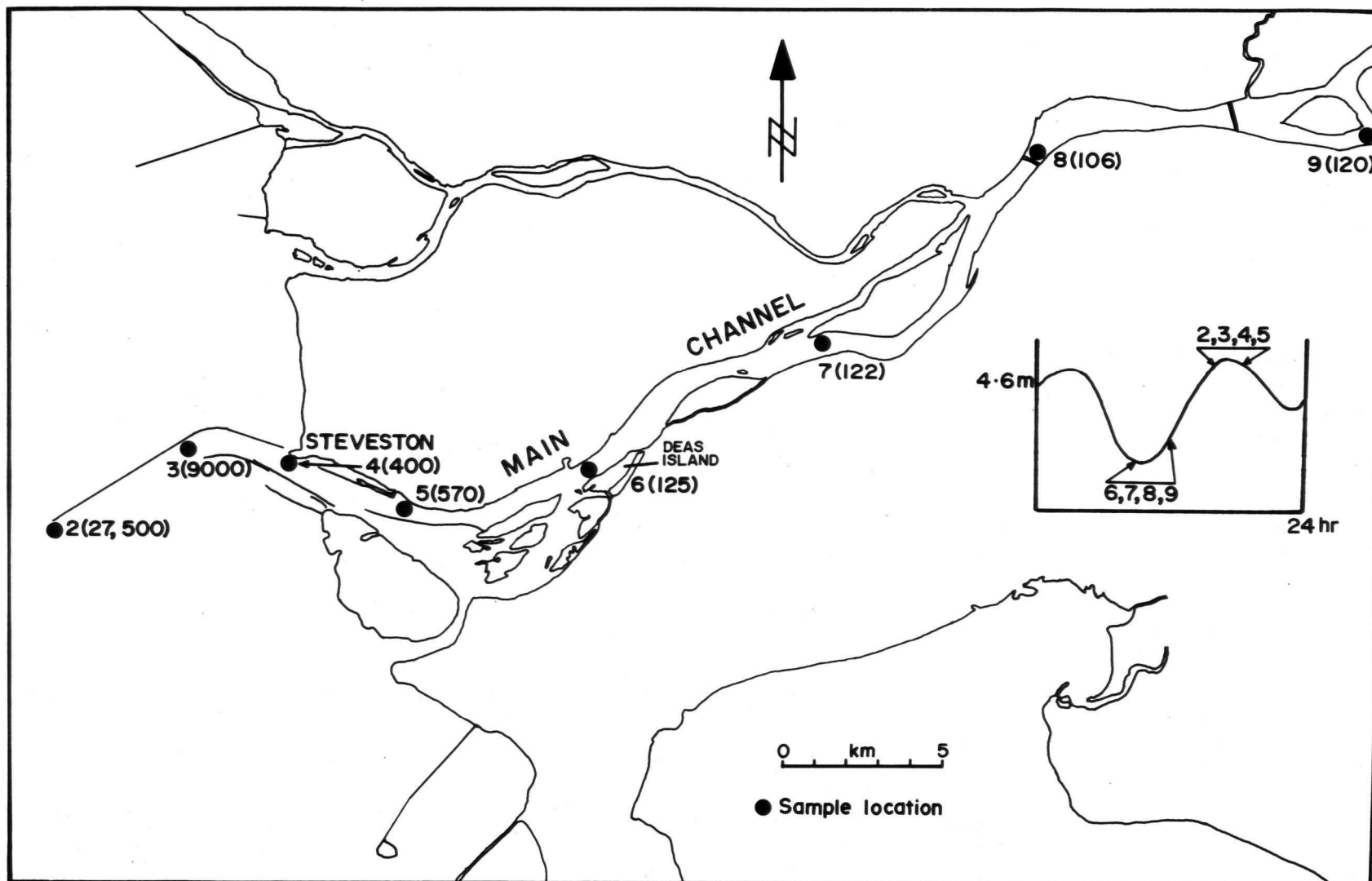


Figure 18: Sampling stations in the Fraser River with conductivity ( $\mu\text{mho}/\text{cm}$  at 1m depth) in parentheses. Sampling times are shown relative to tidal fluctuations at Vancouver; extremes are progressively delayed upriver up to a maximum of three hours at station 9.

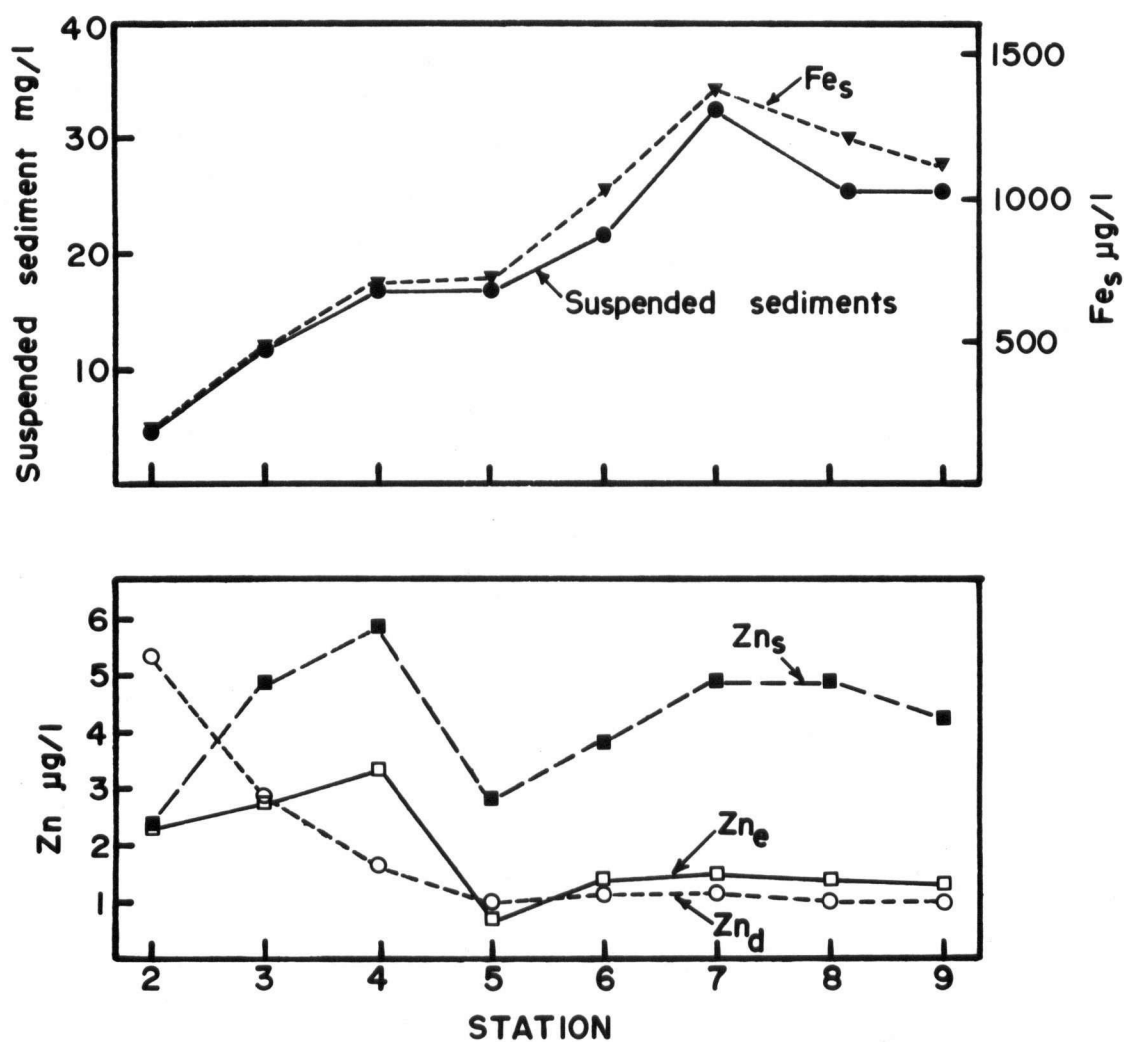


Figure 19: Variations in Fraser River water contents of: suspended sediment; total suspended Fe ( $\text{Fe}_s$ ) and Zn ( $\text{Zn}_s$ ); hydroxylamine hydrochloride-acetic acid-extractable Zn ( $\text{Zn}_e$ ); and dissolved Zn ( $\text{Zn}_d$ ).



<u>Station</u>	<u>Suspended Sediments(mg/l)</u>	<u>Major Elements (ug/l)</u>			
		<u>CaO</u>	<u>MgO</u>	<u>Na<sub>2</sub>O</u>	<u>K<sub>2</sub>O</u>
9	25.7	604	745	337	493
8	25.5	602	783	342	520
7	32.7	759	916	461	611
6	21.6	512	667	279	445
5	16.9	352	466	213	304
4	16.7	337	448	205	294
3	11.7	227	339	162	219
2	4.41	90.4	106	77.2	82.0

Table XVIII: Weight of suspended sediments and suspended major elements in samples from the Fraser River.

Metals

Station	Conductivity(umho/cm)	Zn				Cu			Fe				Mn		
		Zn <sub>d</sub> <sup>a</sup>	Zn <sub>s</sub> <sup>b</sup>	Zn <sub>s</sub> <sup>c</sup>	Zn <sub>e</sub> <sup>e</sup>	Cu <sub>d</sub> <sup>a</sup>	Cu <sub>s</sub> <sup>b</sup>	Cu <sub>s</sub> <sup>c</sup>	Fe <sub>d</sub> <sup>a</sup>	Fe <sub>s</sub> <sup>b</sup>	Fe <sub>s</sub> <sup>d</sup>	Fe <sub>e</sub> <sup>f</sup>	Mn <sub>s</sub> <sup>b</sup>	Mn <sub>s</sub> <sup>c</sup>	Mn <sub>e</sub> <sup>e</sup>
9	120	<1	2.39	165	43	2.6	1.80	69.9	3	1130	4.4	.26	21.5	838	232
8	106	<1	4.89	191	40	2.1	1.92	75.3	3	1210	4.8	.30	23.4	919	257
7	122	1.1	5.83	150	57	2.3	2.06	63.0	6	1370	4.2	.16	27.4	839	188
6	125	1.1	2.82	178	41	2.3	1.59	73.7	3	1020	4.7	.35	19.9	921	290
5	570	<1	3.84	167	31	2.2	1.20	71.2	3	723	4.3	.29	13.8	819	275
4	400	2.6	4.91	349	190	2.7	1.59	95.3	3	690	4.1	.35	13.3	794	313
3	9000	2.9	4.87	418	219	2.6	1.07	91.3	<1	523	4.5	.43	9.34	798	310
2	27500	5.3	4.24	542	464	3.1	.595	135	<1	188	4.3	.30	3.78	858	289

a dissolved metal in ug/l

b particulate metal in ug/l

c particulate metal in ppm sediment

d particulate Fe in % sediment

e HHA-extractable particulate metal in ppm sediment

f HHA-extractable Fe in % sediment

**Table XIX:** Conductivity at 1m depth, and dissolved, total particulate, and HHA-extractable particulate metal concentrations in the Fraser River.

also increase in passing from fresh ( $\leq 1$  to  $1.1\text{ug/l}$ ) to brackish waters ( $2.6$  to  $5.3\text{ug/l}$ ). Thus total Zn ( $\text{Zn}_s$  plus  $\text{Zn}_d$ ) increases from less than  $3.8\text{ug/l}$  to  $8.4\text{ug/l}$  between stations 5 and 4, and remains at  $7.8$  and  $7.7\text{ug/l}$  at stations 3 and 2 respectively. Similarly total Cu increases from  $3.4$  to  $4.3\text{ug/l}$  between stations 5 and 4, reflecting a change in  $\text{Cu}_d$  from  $2.2$  to  $2.7\text{ug/l}$ , and a change in  $\text{Cu}_s$  from  $1.2$  to  $1.6\text{ug/l}$  ( $71$  to  $95\text{ppm}$  dryweight). At the same time  $\text{Fe}_s$  and  $\text{Mn}_s$  remain constant, while, below station 4,  $\text{Fe}_d$  decreases from  $3\text{ug/l}$  to  $<1\text{ug/l}$ . Samples of the saline wedge contain  $1.4\text{ug/l}$   $\text{Zn}_d$ ,  $2.1\text{ug/l}$   $\text{Cu}_d$  (average) and  $<1\text{ug/l}$   $\text{Fe}_d$ .

HHA-extractable Zn levels (Table XIX) indicate that there is a five-fold increase of exchangeable and hydrous oxide-associated Zn in passing from fresh waters (average of  $42\text{ppm}$   $\text{Zn}_e$ ) to brackish waters (more than  $200\text{ppm}$ ) with the greatest increase occurring between stations 5 and 4. This increase ( $2.7\text{ug/l}$ ) appears to account for increase in total suspended Zn ( $3.0\text{ug/l}$ ). Changes in  $\text{Zn}_e:\text{Zn}_s$  are from  $20\%$  in fresh waters to  $50\%$  at stations 4 and 3, and to  $86\%$  at station 2. Five percent of total suspended Fe and  $25\%$  of the Mn are also extracted from suspended sediments in fresh waters, with a slight increase in  $\text{Fe}_e:\text{Fe}_s$  and  $\text{Mn}_e:\text{Mn}_s$  between stations 5 and 4 ( $6.9$  to  $8.5\%$  and  $34$  to  $39\%$  respectively).

## Discussion

### Sorption and Desorption of Zinc

Assuming an average concentration of  $170\text{ppm}$   $\text{Zn}_s$  for river-borne sediments, up to  $50\%$  and  $70\%$  of the total associated with suspended sediments at stations 4 and 2 respectively, might

have become associated with particulates (sorbed) within the channel. This agrees well with changes in  $Zn_e:Zn_s$  (20% in fresh-water to 50% at station 4 and 86% at station 2). The mechanism producing this new association is not immediately obvious, especially considering the simultaneous increase in dissolved Zn values. Sediment Zn and dissolved Zn concentrations in the saline wedge are low (above), suggesting that simple mixing with underlying saline water is not producing the observed effects. Neither can sorption-desorption processes alone account for both increased particulate and dissolved Zn downstream of station 5.

However, assuming sorption does occur, if a mechanism existed whereby suspended sediments have a longer residence time in this region than fresh water,  $Zn_s$  could increase to a greater extent than predictable from total metal contents of the river water. A suitable mechanism may exist, resulting from the tidal influence on river flow, and the stratified flow system developed during intrusion of the salt wedge (p. 14). For example, considerable amounts of sand are resuspended on ebb tides in the lower reaches of the river (Milliman, in press), and a small amount of silt-plus-clay was also observed to be resuspended. Deposition and resuspension will increase the residence time of some particles in the channel. A further delay might be caused by the two-layer stratified flow system, resulting in alternate net seaward and landward movement of particles travelling first in the surface layer and then in the subsurface layer, although this has not been demonstrated. The region between stations 5 and 4 was the site of ebb tide resuspension of bed load at the time the study was

undertaken (Milliman, in press) and was likely near the upstream limit of the saline intrusion. Presence of resuspended material in sample 4 is uncertain. However, the similarity of suspended sediment contents of the two samples (Fig. 19) suggests the normal sedimentation rate upstream has been interrupted, perhaps implying presence of particles delayed in their seaward transport.

Sorption of metals by organic and inorganic particles in saline waters has been demonstrated (Krauskopf, 1956; Kharkar et al, 1968). Freshly precipitated hydrous iron oxide has been shown to be an effective metal sorbant (Kharkar et al, 1968), consistent with its metal scavenging ability in various environments (q.v., Lee, 1975; Jenne, 1968). Since dissolved iron is removed from solution in brackish water between stations 4 and 3, and since the newly sorbed Zn is soluble in HHA (adsorbed or incorporated in hydrous oxides), it is proposed that Zn is scavenged from solution by freshly precipitated hydrous iron oxides. As precipitation of these oxides likely takes place on suspended particles (Aston and Chester, 1973), the combined effects of Zn scavenging and particle retention in the channel could account for greatly increased suspended Zn concentrations. The process probably occurs in a relatively narrow zone at the transition from fresh to brackish conditions; since fresh supplies of river-borne dissolved Fe and Zn are required. Scavenged Zn is probably preferentially associated with fine sediment fractions, as suspended Zn (in ppm sediment) increases as sediment load decreases from stations 4 to 2.

Removal of dissolved iron in other estuaries (Boyle et al, 1974; Holliday and Liss, 1976; Coonley et al, 1971; Bowers et al, 1974; Lowman et al, 1966) has been suggested as a factor in controlling trace metal behaviour in coastal waters (Sholkovitz, 1976; Eisma, 1975; Aston and Chester, 1973; Lowman et al, 1966) but data providing evidence for trace metal scavenging are scarce. Burrell (1973) described the increase of sorbed Zn values on sediments settling through the halocline of an Alaskan fjord, and suggested coprecipitation with iron as a possible mechanism. Precipitation of trace metals and iron in filtered Puerto Rican river waters mixed with filtered sea waters was described by Lowman et al (1966), with the results used to explain iron and trace metal distributions in nearshore sediments. A similar experiment by Evans and Cutshall (1973) with Columbia River water produced no precipitation of metals.

Some authors have suggested that "dissolved" iron carried by rivers is already in colloidal form, and thus its apparent precipitation in estuaries is due to coagulation of particles which previously would pass through filtration apparatus (Coonley et al, 1971). This colloidal phase probably contains trace metals, and its flocculation would therefore cause an apparent increase of particulate metal and decreased dissolved metal concentrations. This process could not, however, account for simultaneous increases in particulate zinc and dissolved zinc values as observed here. The same argument applies to coagulation of metal-complexing organic colloids as an explanation for increased suspended zinc concentrations.

Increase in dissolved zinc concentrations from stations 4 through 2 (Fig. 19) is consistent with reported desorption of metals from river sediments in saline waters as described from field (Fukai et al, 1975; Evans and Cutshall, 1973; de Groot, 1973) and experimental studies (Murray and Murray, 1973; Kharkar et al, 1968), including work in Georgia Strait (Thomas, 1975). Higher dissolved zinc values may thus represent desorption caused by salinity increases resulting from mixing with underlying saline water. Alternately upstream convection of brackish surficial Georgia Strait water (Hodgins, 1974), which, resulting from desorption from suspended or bottom sediments at higher salinities within the Strait, contains higher zinc concentrations than the river at this time of year (Thomas, 1975), might produce increased dissolved zinc concentrations. Thomas observed maximum dissolved zinc values associated with water of salinities of 25 to 28‰. This contrasts with a maximum desorption at 5‰ in the Columbia River estuary (Evans and Cutshall, 1971). Nevertheless, either in brackish waters within the channel, or at higher salinities in Georgia Strait, by some method zinc is mobilized from suspended sediment.

The mechanism of mobilization is not known. Thomas (1975) suggests that zinc (and copper) in exchange sites may be replaced by divalent magnesium and calcium ions in sea water. Trace metal adsorption, however, involves a specific surface reaction, and not simple cation exchange (O'Connor and Kester, 1975), and thus desorption is not a simple exchange process. The process is further complicated by the fact that transition metals in

natural waters predominantly exist not as divalent ions, but as ion pairs and complexes with various organic and inorganic ligands (Zirino and Yamamoto, 1972; Sylva, 1976), and thus adsorbed species will be similarly complexed. Organic complexation may, however, aid desorption by increasing the solubility of metals in marine as compared with riverine conditions (Duursma and Sevenhuyzen, 1966; Rashid and Leonard, 1973). Complexation by organic chelators, chiefly fulvic acids, has been postulated as the cause of apparent desorption from bottom sediments in the Rhine and Ems estuaries (de Groot, 1973).

Data of dissolved and particulate copper behave similarly to those of zinc, although trends are not nearly so well defined. Copper is therefore believed to undergo similar sorption and desorption processes, the latter process having been substantiated by Thomas (1975). Interpretation of manganese behaviour is difficult without dissolved concentrations. Increase in  $Mn_e:Mn_s$  between stations 5 and 4 suggests manganese is adsorbed or coprecipitated with iron. Precipitation of hydrous manganese oxides would be expected to contribute to trace metal scavenging (Graham et al, 1976; Jenne, 1968).

Relative importance of the sorption and desorption processes may be estimated approximately with data from this study and that of Thomas (1975). Assuming sorption of zinc occurs only between stations 5 and 4, suspended sediment is capable of taking up 160 mg/kg zinc, based on the increase in HHA-extractable zinc between these two stations. Integrating records of mean discharge and suspended sediment load at Hope over the freshet period (May through July) of 1973 (Thomas, 1975), a freshet suspended sedi-



ment load of  $11.7 \times 10^9$  kg was discharged, which was capable of sorbing  $1.9 \times 10^9$  g of zinc. Thomas predicts freshet-desorbable zinc to be  $2 \times 10^9$  g, assuming 88ppm zinc is removable from river suspended sediment (based on experimental data). This figure is probably high as results here suggest that the potential for new dissolved zinc must be less than 40ppm, the amount of HHA-extractable zinc in river suspended sediments.

To a first approximation, therefore, sorption of zinc on suspended sediments occurs to at least twice the extent of desorption. Sorption probably occurs predominantly at low salinities where iron first precipitates, while desorption occurs over a range of salinities. It is impossible to estimate what portion of desorbable zinc was originally sorbed onto suspended sediment in the estuary, without separating adsorbed and Fe and Mn oxide-associated zinc from suspended samples of the channel and Georgia Strait. It is interesting to note, however, that metals adsorbed onto freshly precipitated hydrous iron oxides were not desorbed extensively by sea water in experimental studies (Kharkar et al, 1968).

In general, previous studies have stressed the importance of either trace metal sorption or desorption, generally the latter, as sediments enter the ocean. This study may be the first to describe occurrence of both. The apparent uniqueness of the situation in the Fraser may be attributable to the failure of other workers to consider all aspects of the problem. For example, consideration of dissolved concentrations alone will not allow detection of more than one process, as in the case of Georgia Strait (Thomas, 1975), the Var estuary (Fukai et al, 1975) and the

Columbia estuary (Evans and Cutshall, 1973), where desorption has been described. Sampling of bottom sediments only led de Groot (1973) to postulate a desorption mechanism. Decreased metal values moving downstream in the tidal region of the Rhine may, however, be explicable by mixing of river bottom sediments and coastal sediments (Muller and Forstner, 1975), as observed in the Elbe River. Various experimental techniques have also led to artificial results. For example, river-bottom sediments have been used in experimental studies to investigate release of metals on mixing with sea water (Thomas, 1975; Johnson et al., 1967). Results of these experiments must be interpreted cautiously for two reasons: i) bottom sediments are not typical of the total river sediment load; and ii) fresh water sediments are far from being at equilibrium with sea water, and any chemical reactions will appear unrealistically rapid and extreme compared with natural mixing reactions. Thomas' (1975) estimation of 88ppm desorbable zinc, for example, has been shown in this study to be an unrealistically high value for river suspended sediments. Even more artificial results are obtained by mixing particulates which have adsorbed metal from fresh water, with sea water (Kharker et al., 1968; Murray and Murray, 1973). Resulting desorption is not surprising considering how loosely bound are metals adsorbed in this fashion. Furthermore both sorption and desorption in these experiments will occur in response to ambient metal concentrations (O'Connor and Renn, 1964) and may reflect only achievement of equilibrium between dissolved and adsorbed metals. Moreover,

experimental procedures may not duplicate interaction of natural organic materials, which affect both sorption and desorption of metals (Murray and Meinke, 1974; Sholkovitz, 1976).

In the case of the present study, a relatively complete picture of sorption-desorption processes affecting zinc in the Fraser has been gained by considering data of both dissolved and particulate phases of metal transport in conjunction with physical processes.

#### Influence of Sorption-Desorption Processes on Trace Metal Content of Delta-Front Sediments

Sorption of zinc in the hydrous oxide phase of suspended sediment is very likely reflected in HHA-extractable zinc values in delta-front sediments (Chapter IV). The hydrous oxide-associated form of zinc in surficial sediments comprises between 15 and 20% of total zinc values (Tables X and XII). It is not possible to estimate precisely how much of this zinc reflects Fe and Mn oxide scavenging in the channel as opposed to scavenging in weathering and stream environments, as the degrees to which different grain size materials are affected by sorption and desorption processes are not known.

As the scavenging also involves copper, it is likely that some of the HHA-extractable copper in delta-front sediments first became associated with sediment in the main channel. This is consistent with observed similar behaviour of Zn, Cu and Pb in experimental conditions (Krauskopf, 1956), especially regarding their affinity for adsorption to particles, including iron and

manganese oxides. Lead, which occurs overwhelmingly in HHA-extractable form in delta-front sediments, is therefore also believed to be scavenged in the channel, and lead contents of delta-front sediments are expected to reflect this process.

Manganese, as stated previously, may be precipitated (or coprecipitated) as a hydrous oxide in the channel, and may be a scavenging agent for trace metals. Precipitation of manganese would have a small effect on HHA-extractable levels from suspended sediments, however, as this form of manganese is already present on sediment in much greater amounts (Table XIX). Therefore, only a small fraction of manganese hydrous oxide in delta-front sediments is believed to represent material precipitated in the estuary. Similarly, iron hydrous oxide levels in river suspended sediment are little enhanced by precipitation of fresh material in the water column of the channel (Table XIX).

HHA-extractable levels of cobalt and nickel are 15 to 20% and 10% respectively of total values in delta-front sediments. It is not possible to estimate the amount of these metals scavenged in the estuary, although Gibbs' work on suspended sediments of the Yukon and Amazon Rivers (1973) suggests that river suspended sediments contain high proportions of these metals (between 30 and 50% of total concentrations) in association with hydrous oxide coatings. The effect on these metals may therefore be fairly minor.

Total and  $\text{MgCl}_2$ -extractable metal levels of delta-front sediments are expected to be influenced by desorption of metals.  $\text{MgCl}_2$ -extractable metals may be low as a result of desorption of surface-sorbed metals from suspended sediments in Georgia Strait

or on the delta-front (Thomas 1975). The effect the combined processes have on total metal contents of delta-front sediments is not predictable. Considering the high proportion of lattice-bound metals in delta-front sediments, and the fact that sorption and desorption are roughly comparable in magnitude, the overall effect on total metal deposition at the delta-front may not be great. The processes probably do, however, affect the relative proportions of different forms of metal deposited, tending to increase the HHA-extractable metals and decrease the  $\text{MgCl}_2$ -extractable metals. As HHA-extractable metals are unavailable for prediagenetic release, the effect may be temporary net removal of a portion of biologically available metal from the environment.

## CHAPTER VII: MECHANISMS OF TRACE METAL DEPOSITION IN NEARSHORE SEDIMENTS

### Introduction

Similarity of trace metal contents of sediments of the Fraser delta-front and other nearshore regions (Table XIII), suggests common mechanisms affect metal deposition. Some of these mechanisms may be applied to explain retention in nearshore sediment of trace metals introduced by rivers and industries.

### Discussion

#### Trace Metal Deposition in Nearshore Sediments

Average total trace metal contents of unpolluted nearshore sediments low in clay content are remarkably consistent (Table XIII). It follows that, ignoring fjords and other reducing basins, mechanisms of trace metal deposition in nearshore sediments probably do not differ greatly between different regions.

Trace metal deposition on the Fraser delta-front can be briefly generalized on the basis of results of this study (Chapters IV, V and VI). The bulk of Co, Cu, Fe, Mn, Ni and Zn (but not Pb) are transported to the delta-front and deposited as constituent cations in crystalline detrital minerals. A further contribution of metals, including Pb, is present in amorphous grain coatings of hydrous iron and manganese oxides developed during weathering. This fraction is enhanced by

metal scavenged in the estuarine portion of the main channel by newly-formed hydrous iron (and possibly manganese) oxides. A certain amount of adsorbed metal is mobilized in brackish water in the main channel and/or Georgia Strait, and possibly on the tidal flats (Thomas, 1975). After burial, another small fraction of total metals may be mobilized.

Occurrence of processes described here in other near-shore regions is generally confirmed in the literature. Near-shore sediments are known to contain a greater proportion of their trace metal content in detrital minerals than oceanic sediments (Chester and Messiha-Hanna, 1970) because sedimentation rates are highest in nearshore regions. Importance of this fraction in fine sediments from Los Angeles Harbour (Gupta and Chen, 1975) and Severn estuary (Chester and Stoner, 1975) is demonstrated in Table XV. Fe and Mn oxide phases also contain significant proportions of trace metals at these locations (Table XIV), although source of the oxides in these cases was not investigated. Scavenging by hydrous iron oxides, as described in the Fraser estuary, has not been proven elsewhere, although it has been suggested in a number of instances (q.v., Lowman et al, 1966; Burrell, 1973). Loss of adsorbed metals has often been described (q.v., Fukai et al, 1975; Evans and Cutshall, 1973), and mobilization of metals from buried sediments is also a well known phenomenon (q.v., Duchart et al, 1973; Elderfield and Hepworth, 1975).

Other factors, especially organisms and organic matter, also greatly influence metal deposition in nearshore sediments (q.v., Schutz and Turekian, 1965; Rashid, 1974; Nissembaum and Swaine, 1976). Nonetheless, processes observed in this study

appear to be major controls on trace metal deposition in other nearshore regions.

### Trace Metal Sorption in Nearshore Waters

Trace metals, like all dissolved constituents entering the oceans, have a finite residence time in the water column before they are deposited with sediment. Copper, for example, has a residence time of 50,000 years (Goldberg, 1965), a relatively short period compared with residence times of the major cations sodium ( $2.6 \times 10^8$  years) and potassium ( $1.1 \times 10^7$  years). In the case of most trace metals residence times are not governed by solubilities, as they are greatly undersaturated with respect to seawater (Krauskopf, 1956). Furthermore, seawater contains, on the average, smaller concentrations of dissolved metal than incoming river waters (Table XX). In other words, effective mechanisms exist to remove trace metals from solution long before their concentrations become high enough to precipitate salts of the major anions. The most important of these mechanisms include: i) adsorption onto colloidal and fine suspended particles of clay minerals, amorphous iron and manganese oxides, and organic material; ii) coprecipitation with hydrous iron and manganese oxides; iii) precipitation in sulphide minerals; and iv) incorporation in living organic matter and decay products (Goldberg, 1954, 1965; Krauskopf, 1956; Turekian, 1965, 1971; Nissembaum and Swaine, 1976).

Krauskopf (1956) considered adsorption the most effective mechanism controlling levels of rare metals in sea water. As the process depends on the presence of suspended particles, it occurs predominantly in coastal regions, especially



Element	Oceans			Rivers	
	Goldberg (1965;Table I)	Rosler and Lange (1972;Table 97)	Durum and Haffty (1963,Table 4)	Turekian (1971;Table 2.6)	Durum and Haffty <sup>b</sup> (1963;Table 1)
Co	0.1 ug/l	0.1 ug/l		.2 ug/l	0-5.8ug/l(0) <sup>a</sup>
Cu	3	1-90	1-10 ug/l	.9-12	0.83-105(5.3)
Fe	10	2-20			31-1670(300)
Mn	2	1-10		4-12	0-185(20)
Ni	2	.1-.5	.1-.5	0.3	0-71(10)
Pb	.03	4-5	3-4	2.3-3.9	0-55(4.0)
Zn	10	5-14	5-10	5-45	0-215(0)

a median values

b North American rivers

Table XX: Compilation of published summaries of trace metal concentrations in ocean and river waters.

near river mouths (Chester, 1965). Coprecipitation with hydrous iron and manganese oxides has long been known as an effective scavenging mechanism for trace metals in oceanic basins with low sedimentation rates, and occurs during formation of manganese nodules (Goldberg, 1954). The process has also been suggested as a trace metal removal mechanism in nearshore environments (Chapter VI; Eisma, 1975; Sholkovitz, 1976; Burrell, 1973; Lowman et al, 1966). Precipitation of metal sulphides occurs locally in anoxic basins with restricted circulation, as commonly exist in coastal inlets and basins. Uptake of metals by organisms and organic material is greatest in areas of highest productivity, that is, in nearsurface waters, especially near continental margins.

In light of these mechanisms, it is probable that river-borne metals are predominantly removed from solution in nearshore waters (Chester, 1965). This furthermore implies their deposition near to their point of input to the oceans. Turekian (1971) goes so far as to say that most river-borne metal does not leave the estuaries, being removed by organisms, and ultimately fixed as sulphides in the sediment. While removal by organisms is not the only effective process, his overall conclusion is probably valid.

Given the wide range of conditions both within and between estuaries, understanding of this portion of metal cycles will be a complex problem. No doubt solutions to the problem will vary between different geographic localities. Examples of such disparity are already common in the literature. Iron, for example, has been shown to act conservatively in some estuaries

(Eisma, 1975) while behaving in a nonconservative manner in others (Boyle et al, 1974; Coonley et al, 1971; Lowman et al, 1966; Bowers et al, 1974). Zinc, while displaying nonconservative behaviour in the Fraser estuary (Chapter VI; Thomas, 1975) and the Columbia estuary (Evans and Cutshall, 1973) behaves conservatively in the Beaulieu estuary (Holliday and Liss, 1976). Moreover the salinities over which chemical changes occur appear to differ between different localities. Maximum zinc desorption, for example, was described at 5‰ in the Columbia estuary (Evans and Cutshall, 1973) but at 25 to 28‰ in Georgia Strait (Thomas, 1975). Another source of inconsistencies in metal behaviour in estuaries involves differences in pH contrast between river and marine waters. Increasing pH, as usually found in estuarine transition, favours adsorption of metals (Murray and Murray, 1973), countering the desorption effect predicted during increasing salinity at constant pH (O'Connor and Kester, 1975). Another even more obvious variable is the relative metal content of river and coastal waters. In the case of an Alaskan fjord (Burrell, 1973) sediment settles through a sharp halocline into water of greater dissolved zinc concentration, and in response sorbs zinc from solution. Biological uptake (q.v., Turekian, 1971), organic complexation (q.v., Rashid and Leonard, 1973) and physical processes (Chapter VI) also influence the net behaviour of a metal being introduced to the marine environment.

#### Removal of Waste Trace Metals to Nearshore Sediments

Trace metals of industrial and urban origin discharged into rivers and nearshore waters may be at least temporarily

removed from the water column by sorption processes. Results of this study (Chapter VI) suggest some estuaries have a certain capacity to sorb dissolved metals and thus render them unavailable to marine organisms. Removal of waste metals to sediment has been observed in the Back River estuary (Helz et al, 1975), and experimental addition of metals to salt marsh ponds was almost all accounted for by enrichment of metals in sediment (Duke et al, 1966). Metal sorption capacity will be surpassed at certain levels of contamination, in which case trace metals will be transported to deeper waters and/or ingested by marine organisms. Even metal removed to sediments, however, is not permanently inaccessible. Post-burial mobilization, in combination with current activity or dredging operations, will reintroduce dissolved metals to the water column (Duincker et al, 1974; Elderfield and Hepworth, 1975).

## CHAPTER VIII: CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

Summary of Conclusions

- (1) Trace metal contents of Fraser delta-front sediments are typical of other nearshore unpolluted sediments. They display an inverse relation with sediment grain size, as commonly observed elsewhere.
- (2) Trace metals in delta-front sediments reside largely within lattice sites of detrital minerals, with a sizeable fraction bound in amorphous hydrous oxides of Fe and Mn. Pb is an exception to this rule, being extracted almost exclusively with the latter phase. Adsorbed metals (excepting Mn) are insignificant over the delta-front as a whole, except in the region affected by discharge of primary treated sewage from Iona Island. This region displays total contents of Cu, Pb and Zn which are anomalous.
- (3) Trace metal profiles of short cores are generally uniform, except in those cores containing textural variations. Apparent loss of some metals at depth may reflect post-depositional mobilization, assuming metal input rates to the delta-front have been constant over the time represented within the cores. This assumption is suspect, as at least one area (near Iona Island) contains a nearsurface transition in metal concentrations related to urban activities.
- (4) Scavenging of dissolved zinc from the water column by newly formed iron (and possibly manganese) hydrous oxide coatings occurs in brackish waters of the main channel. This sorption

process probably accounts for a fraction of trace metal contents, especially Cu, Pb and Zn, of delta-front sediments. Desorption of Zn also takes place in the channel or Georgia Strait, but to a somewhat lesser extent than the sorption process.

(5) Processes similar to those described here probably affect trace metal deposition in other nearshore sediments. Sorption processes partially account for retention of dissolved metals, including contaminant metals, in nearshore sediments.

#### Suggestions for Further Research

Additional research projects suggested by results of this study include:

- (a) extension of sediment sample collection and analysis to deeper portions of the delta-front and Georgia Strait;
- (b) characterization and determination of metal content of the organic fraction of fine-grained sediments, especially in areas receiving sewage discharge;
- (c) collection of longer cores in regions of continuous deposition, application of a suitable dating technique to determine sedimentation rates, and analysis of extractable and total metals of sediments, and dissolved and complexed metals within interstitial waters;
- (d) river water and suspended sediment sampling at different times of year, over tidal cycles and at several depths, and analysis for extractable and total particulate, and complexed and total dissolved metal; and
- (e) collection and analysis of water and suspended sediments

within the plume and at surface and bottom depths over the delta-front.

Any future work done in this area, or in fact in any other area, should examine as many phases of metal association as possible. Total and partial extracts of metals in water, suspended sediment, surficial sediments, subsurface sediment, interstitial water and biomass would provide a more complete picture of trace metal behaviour in nearshore regions.

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## APPENDICES

## APPENDIX A

CO, CU, FE(%), MN, NI, PB AND ZN CONTENT (PPM) OF FRASER DELTA-FRONT SEDIMENTS

## SERIES A INTERTIDAL SAMPLES (FEBRUARY 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN	%LI	%SAND
1	124	61	9.94	14.12	1.52	272.19	38.36	3.07	41.31	1.1	96.9
2	136	62	9.98	14.98	1.64	299.89	42.90	4.24	43.18	2.1	94.2
3	149	59	13.26	30.95	2.29	323.94	46.24	9.18	63.48	3.9	34.0
4	148	49	11.37	22.74	2.38	286.40	41.56	3.95	62.07	3.2	50.0
5	134	45	11.09	16.49	1.81	313.11	39.78	4.87	50.07	2.7	80.3
6	124	50	10.23	22.21	1.66	305.81	45.98	1.31	39.41	1.6	95.3
7	111	49	11.72	12.38	1.81	315.68	47.95	1.31	40.80	1.7	96.1
8	111	37	8.71	12.41	1.49	287.94	36.39	2.82	38.79	1.0	94.8
9	123	37	10.39	13.05	1.83	282.50	47.22	0.94	42.32	1.3	98.2
10	137	38	10.66	14.40	1.86	303.75	38.86	2.44	47.65	1.5	88.6
11	150	37	11.68	16.13	2.08	298.93	41.61	3.73	52.04	2.5	67.5
12	162	37	10.70	16.22	2.10	359.85	38.41	3.89	56.02	3.9	67.5
13	151	26	13.40	13.75	2.25	320.35	58.60	4.43	54.22	1.9	94.2
14	136	26	10.64	13.72	1.89	307.63	40.15	5.35	46.85	1.7	94.7
15	123	25	10.31	15.09	1.72	295.09	43.78	3.20	45.72	1.1	92.3
16	112	25	10.33	12.20	1.68	290.68	43.78	0.0	42.17	1.1	96.8
17	95	35	8.32	11.94	1.53	269.17	38.96	0.0	38.85	0.7	96.1
18	162	13	14.62	10.51	2.36	320.72	77.25	0.25	51.28	0.8	95.5
19	165	22	8.57	10.44	1.75	199.71	33.92	1.66	44.98	2.2	95.3
20	174	24	12.15	16.05	2.08	232.50	41.38	2.10	57.39	3.1	76.5
21	174	36	11.37	16.44	2.12	243.91	40.95	3.29	59.79	3.2	65.8
22	159	49	12.97	30.72	2.37	307.67	47.91	7.99	79.75	2.8	30.4
23	73	43	15.17	40.50	2.45	364.56	53.91	9.48	76.19	2.6	8.3
25	123	88	11.25	14.37	1.86	335.87	54.86	2.23	46.30	0.0	94.9
26	121	94	14.28	36.28	2.53	342.70	50.79	62.91	72.28	2.2	22.9
27	111	100	10.40	16.53	1.72	457.18	42.77	2.04	47.08	1.0	92.4
28	111	88	12.22	22.86	2.06	411.60	44.22	6.79	57.02	1.6	80.7
29	105	73	10.76	14.83	1.71	436.93	39.70	3.68	46.36	0.8	92.6
30	120	73	11.90	17.59	1.89	365.45	41.68	4.75	50.92	1.2	85.9
31	110	62	11.44	16.13	1.71	403.63	41.27	3.82	50.59	1.1	84.5
32	95	80	12.99	27.83	2.31	340.83	45.59	8.41	64.61	2.7	62.1
33	85	87	9.23	16.68	1.63	278.78	37.10	2.67	43.95	1.4	95.0
34	85	75	14.08	12.27	2.13	355.39	62.81	3.91	53.43	0.0	96.9
35	85	56	9.84	12.40	1.58	286.55	39.55	2.72	45.41	0.1	95.3
36	101	56	9.70	13.29	1.57	298.87	37.76	3.06	43.33	1.4	96.0
37	72	76	12.43	13.32	1.86	358.94	57.68	0.0	50.06	1.4	95.1
38	74	101	12.74	12.55	1.82	325.18	49.71	1.25	47.21	1.4	95.9
39	83	117	11.06	11.79	1.73	276.02	45.08	3.22	44.34	1.2	94.2
40	81	127	13.77	12.40	2.00	318.98	59.99	3.61	50.42	1.9	88.9
41	80	140	12.72	12.52	2.01	311.50	53.68	3.14	48.57	1.6	95.6
42	79	153	10.84	14.28	1.69	296.16	41.06	3.33	48.83	1.4	86.4
43	79	166	12.72	13.79	1.89	318.13	48.71	5.04	53.10	1.3	94.8
44	82	182	10.71	13.88	1.66	247.23	37.05	5.01	47.60	1.4	95.5



45	86	199	10.48	13.18	1.60	232.05	35.84	4.32	47.01	2.2	96.3
46	89	209	10.35	14.11	1.64	522.35	40.59	0.0	47.57		
47	99	199	10.47	13.03	1.69	283.88	37.48	1.51	49.15	1.9	94.7
48	99	186	9.71	14.56	1.76	339.00	30.15	9.31	51.68	1.9	92.7
49	112	192	11.38	24.46	2.11	285.85	41.00	10.81	67.58	3.2	54.1
50	123	117	11.57	21.46	2.07	290.83	38.55	5.66	63.72	3.6	31.3
51	124	131	11.00	19.23	1.85	291.07	37.76	5.63	60.60	1.9	62.1
52	123	145	12.48	22.77	1.97	285.61	40.42	5.75	62.85	2.5	48.6
53	121	156	12.07	23.16	1.95	312.89	39.77	10.88	64.90	2.5	60.6
54	118	184	10.03	42.65	1.59	193.68	34.67	38.88	83.40	3.0	67.2
55	111	175	15.04	47.16	2.45	375.09	47.57	29.13	94.82	5.6	52.3
56	111	162	10.81	14.53	1.54	284.46	37.19	3.11	50.48	2.0	91.7
57	111	150	12.59	23.99	2.19	341.59	41.14	8.55	70.38	3.0	58.0
58	111	137	11.30	13.17	1.58	343.83	38.38	5.92	50.44	2.0	93.4
59	111	125	12.47	18.44	1.86	367.25	42.38	6.50	60.11	2.8	81.9
60	95	116	11.84	11.41	1.64	321.90	53.15	1.76	48.62	0.4	96.7
61	86	138	10.22	12.38	1.53	280.08	39.43	3.37	46.94		
62	86	150	9.86	11.35	1.51	239.11	39.29	4.01	45.27	1.5	97.9
63	85	162	10.50	13.06	1.64	276.19	39.91	4.83	56.22	1.3	91.2
64	86	175	12.81	13.12	2.02	366.74	49.80	4.39	53.79		
65	98	175	9.57	12.65	1.47	286.71	32.00	4.55	45.76	2.0	94.8
66	99	161	10.16	12.53	1.71	267.82	42.98	2.49	47.99	0.7	94.1
67	98	150	10.32	13.09	1.66	273.84	40.57	3.00	47.66	1.1	98.5
68	98	138	9.31	12.00	1.64	251.02	38.14	5.30	47.20	0.6	96.7
69	99	124	8.88	10.69	1.57	247.48	41.80	2.92	43.67	1.2	95.4

SERIES B FORE-SLOPE SAMPLES (MARCH 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN	%LI	%SAND
1	61	94	12.63	35.10	2.51	359.98	48.40	18.74	76.49	4.5	40.5
2	54	94	11.88	28.97	2.23	414.48	50.86	15.31	69.98	3.7	57.6
3	49	94	12.42	37.35	2.37	325.85	46.68	15.54	90.78	7.2	30.5
4	49	100	12.94	36.22	2.74	312.48	46.18	9.85	77.73	5.6	22.5
5	54	100	12.65	37.27	2.51	319.80	47.13	17.03	79.69	5.1	37.1
6	61	100	13.21	36.02	2.69	338.72	48.91	12.41	78.47	4.2	33.8
7	64	100	11.84	27.77	2.38	324.88	44.55	10.36	69.52	2.3	35.0
8	67	100	14.00	31.37	2.39	331.95	47.79	7.71	71.52	2.8	33.4
9	67	106	14.93	40.74	3.15	393.35	51.17	11.45	89.05	5.7	18.1
10	61	106	14.47	38.16	2.52	343.42	50.24	16.32	76.63	6.1	26.9
11	54	106	13.39	37.90	2.52	352.16	48.76	13.41	83.56	5.3	30.0
12	36	100	12.81	36.41	2.35	279.56	47.76	8.00	74.70	5.2	24.8
13	23	113	12.17	36.22	2.75	331.95	46.35	7.27	85.63	5.0	19.9
14	23	126	13.55	38.27	3.25	404.92	46.50	14.19	99.26	4.8	16.6
15	36	126	13.04	39.24	3.10	381.55	48.83	8.66	97.60	4.2	13.6
16	36	113	14.03	38.81	2.75	293.57	44.47	8.30	78.07	3.9	20.3
17	49	113	12.77	38.67	2.17	285.70	50.79	10.52	75.52	4.4	27.4
18	54	113	13.89	40.49	2.39	340.11	50.99	15.69	77.07	5.6	25.7
19	61	113	13.09	40.22	2.43	349.16	50.32	22.82	113.89	5.8	25.0
20	67	113	14.08	41.11	2.81	426.60	51.27	17.85	94.29	5.2	19.0
21	70	113	14.56	38.19	3.24	360.32	51.22	11.45	87.35	3.3	19.6
22	73	113	11.73	11.45	1.91	255.31	44.82	3.13	50.72	1.0	96.6
23	73	119	12.07	18.41	2.01	253.20	43.85	7.33	68.02	0.4	72.8
24	70	119	13.97	39.89	2.23	243.53	51.95	14.63	75.75	3.2	18.3
25	67	119	14.40	40.45	2.92	350.90	49.94	14.90	85.87	4.9	18.4
26	61	119	13.98	43.59	2.75	393.31	51.02	13.48	92.09	6.0	18.6
27	49	126	14.69	41.98	2.56	356.66	50.32	10.44	84.12	6.7	13.3
28	61	126	14.40	42.83	3.20	366.02	49.94	9.07	92.37	6.0	10.5
29	67	126	15.38	42.35	3.35	380.65	50.14	13.79	92.37	5.0	15.2

30	70	126	15.04	41.71	2.95	408.98	49.09	11.74	93.01	5.6	19.7
31	73	126	13.70	30.24	2.34	301.17	47.01	3.16	72.45	5.1	45.6
32	73	132	13.22	31.08	2.06	278.14	46.91	9.82	72.19	1.7	55.8
33	70	132	14.92	41.29	2.72	347.54	52.54	10.84	91.06	4.0	19.9
34	67	132	15.27	43.05	2.98	382.46	52.73	13.58	91.97	5.5	14.0
35	61	132	15.21	42.79	3.31	381.94	53.90	12.46	98.26	5.2	10.8
36	49	138	14.58	42.68	3.08	380.65	55.79	13.15	102.56	5.6	10.4
37	61	138	14.40	42.54	3.01	405.23	54.35	6.01	96.79	5.6	9.1
38	67	138	14.35	39.25	2.92	456.51	52.74	18.24	92.26	4.9	15.9
39	70	138	15.64	40.82	2.98	400.45	51.87	15.17	94.25	3.3	16.7
40	73	138	14.30	25.22	2.22	294.33	45.37	11.31	68.93	1.1	59.5
41	73	144	11.54	24.43	2.19	299.45	45.02	9.75	65.51	1.0	54.7
42	70	144	14.10	38.35	2.77	397.62	49.87	18.02	87.85	4.0	22.4
43	67	144	13.86	40.60	2.95	386.14	53.15	16.11	103.42	6.0	16.2
44	61	144	14.62	41.46	3.01	386.54	53.13	14.99	102.79	6.2	9.2
45	49	150	13.76	41.66	3.14	432.90	50.55	16.25	111.20	6.9	9.9
46	61	150	12.44	42.15	2.94	420.38	51.77	15.57	110.68	5.8	12.0
47	67	150	12.15	42.45	2.82	366.23	55.39	14.47	108.79	3.8	15.2
48	70	150	11.67	37.91	2.61	375.08	51.06	14.90	91.46	2.8	29.2
49	73	150	10.67	14.78	1.74	244.53	40.91	5.11	52.30	1.5	84.4
50	73	157	9.65	11.19	1.54	252.97	41.13	3.09	48.59	2.7	96.5
51	70	157	13.90	33.22	2.32	327.77	47.10	14.17	80.89	4.4	41.5
52	67	157	14.40	40.28	2.72	356.70	52.56	13.38	99.83	5.2	21.2
53	61	157	13.54	43.41	2.91	368.04	54.80	13.77	100.99	6.2	11.5
54	49	163	15.74	42.83	2.78	388.53	56.95	15.89	110.47	6.1	8.6
55	61	163	14.72	41.46	2.85	401.93	48.37	15.60	131.52	4.9	17.1
56	67	163	11.83	36.06	2.54	350.07	46.48	14.24	92.83	3.4	25.7
57	70	163	11.61	25.89	2.03	282.77	40.70	9.29	71.93	3.1	52.0
58	73	163	11.81	10.18	2.28	313.67	49.47	4.34	52.30	2.0	98.9
59	73	169	11.09	14.12	1.80	236.24	39.47	5.83	55.46	3.3	86.4
60	70	169	14.65	33.90	2.37	320.43	46.24	12.19	81.67	4.1	40.0
61	67	169	15.95	42.26	2.66	365.66	50.36	13.27	99.70	5.2	19.5
62	61	169	16.55	45.93	2.92	406.88	50.98	14.55	108.86	7.2	8.2
63	49	176	16.78	44.44	2.88	421.86	51.57	14.27	111.56	7.1	8.2
64	61	176	17.12	42.91	2.95	396.54	50.56	14.15	104.08	5.3	9.7
65	67	176	15.30	42.68	2.82	389.37	49.54	14.59	98.05	3.4	15.9
66	70	176	15.62	40.30	2.64	348.88	48.74	14.60	86.94	3.0	19.6
67	73	176	13.37	23.27	2.10	267.45	43.36	6.54	62.96	2.4	65.5
68	73	182	14.00	16.72	1.94	254.55	42.59	5.61	57.32	1.4	82.4
69	70	182	15.45	35.37	2.41	341.86	45.41	16.89	88.13	3.8	35.2
71	61	182	16.42	45.28	2.98	416.52	51.96	16.96	112.64	6.4	7.6
72	49	188	16.59	44.40	3.08	430.16	50.38	16.72	109.29	7.5	0.6
73	61	188	16.48	44.89	3.13	423.79	51.67	17.71	105.72	5.3	3.8
74	67	188	16.23	43.38	2.94	391.49	52.35	16.66	98.62	4.1	6.1
75	70	188	15.47	40.91	2.65	369.13	49.31	16.15	94.61	13.0	12.0
76	73	188	14.38	21.10	2.16	282.41	46.11	8.93	61.43	1.7	50.4
77	80	188	11.98	10.95	1.66	261.66	38.70	5.45	45.06	1.2	79.2
78	80	194	12.95	10.79	1.73	253.54	40.72	6.61	47.34	1.1	59.9
79	73	194	14.44	28.04	2.28	283.69	45.23	10.05	68.80	2.5	26.5
80	70	194	16.93	43.50	2.90	376.65	49.59	16.44	96.49	4.6	5.4
81	67	194	16.77	45.11	2.88	403.97	51.36	16.08	99.91	4.9	4.4
82	49	200	15.39	47.02	3.27	512.50	50.51	22.34	111.93	6.6	0.8
83	61	200	16.31	46.44	2.95	427.47	49.96	18.03	106.89	5.3	5.7
84	67	200	16.15	44.80	2.95	379.29	53.51	15.50	102.48	3.7	0.0
85	73	200	15.21	35.14	2.47	315.41	47.20	11.09	82.81	4.5	22.2
86	80	200	13.43	12.85	1.91	257.24	43.54	3.59	53.10	2.1	57.4
87	80	207	12.86	30.76	2.36	303.63	42.65	11.09	75.53	3.8	31.4
88	76	207	12.77	17.66	2.04	257.80	42.45	5.35	55.11	1.7	49.5
89	73	207	13.65	34.99	2.59	324.41	44.45	12.25	82.58	2.5	12.1
90	67	207	16.21	46.70	3.19	421.53	53.43	17.29	109.02	3.4	7.3

91	61	213	16.63	45.99	3.15	414.00	53.03	20.49	110.34	5.7	3.9
92	67	213	15.65	47.27	3.20	387.30	53.32	18.87	106.38	5.5	8.7
93	73	213	13.67	33.35	2.45	311.66	45.71	12.27	80.02	3.4	17.7
94	76	213	13.71	29.16	2.28	263.92	44.38	10.43	72.32	3.1	29.4
95	80	213	14.46	21.12	2.73	312.75	53.21	6.12	66.77	2.4	48.0
96	80	219	13.51	16.96	2.20	274.56	48.08	6.49	60.30	1.8	50.8
97	76	219	13.24	26.83	2.31	303.75	44.71	11.57	98.80	2.5	33.4
98	73	219	14.16	36.88	2.53	322.09	47.41	13.11	85.24	2.4	16.7
99	67	219	15.63	48.35	3.03	457.82	50.91	23.13	113.44	4.8	8.4
100	61	225	15.81	47.39	3.05	389.42	53.67	23.46	113.48	6.3	7.5
101	67	225	14.93	44.51	2.83	364.13	52.18	16.28	98.96	5.2	10.2
102	73	225	13.47	38.79	2.55	323.40	48.25	15.35	87.34	4.3	20.0
103	80	225	11.28	10.23	1.68	248.32	41.43	3.25	42.90	0.8	56.0
104	86	232	9.98	12.56	1.49	222.61	33.86	5.24	40.98	1.4	63.5
105	86	238	12.42	28.36	2.11	281.76	40.59	14.43	76.75	2.2	19.8
106	80	232	11.32	13.53	1.54	226.70	36.52	3.24	40.50	0.8	83.1
107	73	232	13.43	29.02	2.23	299.01	41.48	12.02	72.50	2.2	32.5
108	67	232	13.68	40.68	2.63	396.60	47.21	21.11	90.68	3.9	18.2
109	80	238	10.69	23.15	1.86	255.89	38.83	10.74	66.97	2.8	43.5
110	73	238	12.38	31.63	2.16	284.65	39.90	14.03	72.31	3.7	32.6
111	67	238	14.77	45.40	2.75	371.63	55.42	20.75	102.50	5.3	13.9
112	61	232	15.34	47.04	2.79	401.92	47.82	25.27	109.05	6.3	22.2
113	61	238	14.52	50.46	2.94	375.63	47.31	32.44	115.82	5.6	11.0
114	49	238	14.95	48.97	2.99	423.86	46.67	35.78	122.09	5.4	7.5
115	61	244	15.19	61.48	2.99	499.28	43.32	43.39	124.43	4.2	9.4
116	67	244	16.64	49.82	2.34	323.64	34.88	19.65	97.83	4.6	14.5
117	73	244	14.03	37.49	2.33	305.99	41.95	16.96	84.32	4.0	22.0
118	80	244	14.40	36.33	2.39	310.64	45.20	13.71	84.92	4.3	18.9
119	86	244	12.94	34.54	2.18	303.02	41.90	12.86	80.94	3.7	22.8
120	92	250	13.04	32.29	2.09	279.58	40.72	13.31	75.17	3.4	29.7
121	86	250	13.68	41.32	2.61	321.46	47.21	15.24	91.65	5.3	13.8
122	81	250	13.58	47.39	2.49	332.18	44.95	23.05	97.38	3.6	17.6
123	73	250	13.53	45.66	2.61	324.44	44.25	20.50	90.71	2.1	14.4
124	67	250	15.07	60.91	2.74	420.95	42.89	48.77	131.76	2.8	12.5
125	61	250	14.77	53.98	2.56	408.36	41.57	33.41	108.00	5.3	16.1
126	67	257	15.40	55.46	2.88	356.52	50.97	26.72	113.98	5.5	10.4
127	73	257	14.74	50.88	2.45	344.21	47.55	22.76	106.17	4.4	15.1
128	80	257	14.74	45.90	2.34	304.02	43.71	21.45	91.39	4.7	12.0
129	86	257	14.77	53.08	2.74	354.59	50.31	25.80	106.09	5.8	8.0
130	92	257	13.49	44.45	2.60	335.33	41.31	21.83	94.06	3.9	10.5
131	92	263	16.19	61.68	2.42	321.58	46.86	22.12	96.35	2.5	4.5
132	86	263	15.87	62.10	3.00	374.29	48.89	36.53	125.50	3.6	4.0
133	162	6	12.15	11.38	2.00	255.72	50.04	1.88	60.15	10.9	60.0
134	155	6	13.51	28.13	2.49	291.00	47.48	5.40	83.05	3.2	14.3
135	155	12	11.36	11.27	1.67	240.13	43.76	2.95	52.11	1.6	68.9
136	148	6	15.50	23.56	2.44	291.95	53.52	5.28	72.74	8.3	34.4
137	143	6	12.81	12.60	2.11	275.34	51.52	1.28	57.02	1.3	62.4
138	143	12	16.45	11.04	2.56	329.55	79.21	1.78	69.62	1.2	64.5
139	143	18	13.10	17.56	1.99	269.72	45.98	3.22	61.24	0.9	41.9
140	136	18	14.81	15.46	2.23	295.56	58.29	4.55	62.15	0.5	55.7
141	136	12	13.99	17.09	2.00	282.42	54.03	2.26	46.66	0.6	83.3
142	136	6	15.27	11.70	2.14	301.11	62.54	2.33	47.74	0.5	98.7
143	130	6	12.00	11.66	1.51	247.72	43.25	1.83	40.77	1.0	97.8
144	130	12	10.57	13.38	1.54	264.60	43.39	1.75	44.29	1.8	93.4
145	130	18	14.78	13.27	2.02	319.85	64.93	1.77	54.49	1.4	93.6
146	123	18	13.94	23.29	1.94	310.33	51.61	4.61	61.51	2.5	64.8
147	123	12	12.06	13.09	1.77	295.29	53.97	3.02	49.94	0.4	97.7
148	123	6	12.78	14.03	1.79	297.24	52.72	3.72	51.42	0.3	88.1
149	117	6	13.01	15.69	2.10	327.46	56.68	3.79	62.63	1.1	84.7
150	117	12	13.12	11.99	1.90	323.53	65.13	2.19	49.70	0.8	97.3

151	117	18	12.70	17.29	2.03	280.64	52.93	3.43	57.39	2.8	89.1
152	111	18	12.48	11.50	1.73	272.24	57.01	2.60	47.64	0.9	98.8
153	111	12	14.13	13.46	1.99	310.92	71.52	1.78	50.51	0.8	96.8
154	111	6	13.22	11.28	2.06	320.21	66.75	2.29	59.73	0.9	98.4
155	98	6	11.81	17.88	2.13	289.92	48.16	9.31	68.95	1.9	73.9
156	98	12	12.50	17.44	2.08	319.14	50.32	4.67	63.88	1.5	76.8
157	86	12	11.36	20.20	1.99	273.58	41.27	5.57	67.01	2.5	68.5
158	73	12	11.27	25.59	2.31	294.25	38.62	9.13	80.90	4.9	52.1
159	98	18	11.87	12.84	1.82	274.92	49.14	2.97	53.50	1.9	90.8
160	104	18	15.86	12.56	2.30	354.92	73.58	1.91	55.06	1.0	98.3
161	110	24	12.84	23.18	2.09	337.31	48.08	6.50	66.68	2.7	71.5
162	108	24	11.85	13.35	1.73	285.04	52.07	4.85	61.65	1.6	96.4
163	105	24	13.41	22.43	2.27	335.02	54.62	6.66	72.67	2.7	75.5
164	105	31	14.97	32.01	2.28	367.38	54.98	6.61	85.76	2.2	42.3
165	98	31	15.51	33.60	2.44	349.19	53.15	5.83	77.54	3.0	40.2
166	98	24	11.93	12.56	1.94	286.66	51.02	1.35	50.96	1.0	94.7
167	92	24	10.92	10.71	1.66	269.67	45.74	2.18	44.82	0.8	97.1
168	86	24	10.38	10.34	1.65	266.16	44.92	0.93	44.59	0.8	95.9
169	73	24	12.02	21.84	2.10	265.48	42.02	5.86	71.69	3.0	62.8
170	61	24	10.60	22.34	2.13	304.72	36.47	8.86	82.06	5.3	51.7
171	80	31	10.12	11.94	1.50	222.66	37.30	2.90	46.39	1.6	95.4
172	86	31	8.69	11.35	1.32	212.32	36.79	2.07	39.80	1.2	99.0
173	92	31	9.45	12.60	1.54	247.81	40.02	2.34	45.56	1.5	97.9
174	95	31	10.71	13.95	1.71	265.36	43.12	2.89	48.41	1.4	95.3
175	92	37	11.81	12.53	1.82	328.54	53.85	2.54	49.33	1.4	98.3
176	89	37	9.70	12.17	1.52	251.25	40.59	2.60	47.13	1.5	98.3
177	86	37	10.85	12.03	1.51	238.25	36.64	1.53	42.04	2.0	95.5
178	80	37	10.99	14.47	1.69	258.61	39.92	4.22	49.46	1.6	91.9
179	73	37	12.26	20.88	2.04	281.34	41.51	5.23	64.10	2.4	70.2
180	67	37	11.30	20.96	1.98	275.48	39.67	11.25	69.14	2.5	63.4
181	61	37	11.37	21.37	2.14	287.58	36.86	7.31	74.49	3.0	55.9
182	67	44	11.44	19.99	1.98	282.49	39.32	4.96	62.67	2.9	70.3
183	73	44	10.98	18.27	1.81	268.19	39.08	2.69	60.34	2.1	80.4
184	80	44	11.84	17.17	1.85	283.88	45.97	2.61	54.49	2.1	79.6
185	83	44	9.60	11.63	1.51	261.64	41.07	1.41	41.90	2.0	99.0
186	86	44	13.20	23.04	2.09	320.64	47.96	4.70	62.21	3.3	74.3
187	80	50	12.74	17.78	2.00	290.85	45.60	3.29	61.47	1.5	81.4
188	77	50	12.56	22.07	2.05	292.01	47.38	3.03	62.38	1.6	73.2
189	73	50	12.65	20.37	2.01	297.50	48.68	3.75	61.93	2.1	72.0
190	67	50	13.02	26.26	2.16	302.66	46.00	4.73	67.27	2.5	58.5
191	61	50	12.38	27.09	2.15	302.78	45.09	5.14	76.37	4.0	52.6
192	54	50	11.07	26.65	2.24	305.02	40.43	10.56	79.20	5.1	47.7
193	48	50	11.91	26.79	2.23	345.08	38.57	10.00	77.22	4.9	45.2
194	54	56	11.98	21.39	2.10	294.11	42.56	7.68	64.98	4.0	68.9
195	61	56	12.21	20.83	1.96	307.74	42.29	6.30	61.82	3.0	77.2
196	67	56	10.61	17.87	1.80	270.80	41.94	2.04	51.97	0.6	87.8
197	70	56	12.65	13.10	2.12	301.84	54.47	3.76	54.99		
198	73	56	15.37	23.91	2.28	334.60	56.38	3.39	70.09	1.9	69.3
199	67	62	12.17	12.57	1.78	297.73	49.35	0.0	47.54	1.4	97.1
200	64	62	11.47	18.66	1.83	288.88	44.06	3.24	53.54	1.6	87.0
201	61	62	11.65	22.52	2.01	295.04	43.36	4.57	59.85	2.3	76.2
202	54	62	14.12	30.71	2.33	344.46	48.22	9.44	76.74	2.3	45.9
203	48	62	12.35	28.21	2.25	335.71	45.12	8.03	81.05	4.3	40.5
204	48	68	13.04	29.47	2.28	377.61	46.97	8.08	81.05	4.9	41.5
205	54	68	10.34	22.11	1.81	307.15	44.34	3.73	58.70	3.3	78.1
207	64	68	12.18	16.20	1.83	315.97	46.09	5.48	52.24	3.0	86.9
208	61	75	13.63	21.76	2.16	347.26	49.82	6.42	59.94	2.2	77.0
209	57	75	11.40	24.08	1.91	301.42	43.12	8.00	57.70	3.3	77.0
210	54	75	11.81	26.01	2.05	344.16	47.12	8.60	65.66	6.2	76.2
211	48	75	12.07	27.64	2.14	337.76	44.89	8.05	70.10	4.6	58.3

212	36	75	10.68	22.63	1.77	290.59	45.31	4.16	53.96	2.9	80.6
213	36	88	13.70	36.20	2.49	355.87	49.90	8.12	85.72	3.0	24.4
214	48	88	13.19	32.51	2.35	376.19	46.51	11.62	92.08	4.0	40.2
215	48	81	11.70	29.89	2.16	326.31	46.06	8.52	75.13	4.2	51.3
216	54	81	11.28	27.44	2.04	318.60	47.10	9.15	65.24	3.6	68.8
217	57	81	12.60	29.16	2.19	329.46	47.84	8.19	70.68	4.1	61.2
218	61	81	10.00	16.86	1.67	288.39	43.78	3.54	44.45	2.1	98.0
219	54	88	11.72	21.84	1.95	394.28	53.02	6.47	55.79	2.2	82.0
220	61	88	12.09	28.23	2.01	333.11	49.50	12.32	63.27	3.1	67.4

SERIES C INTERTIDAL SAMPLES (APRIL 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN
1	159	48	15.08	35.75	2.81	420.89	55.76	8.68	93.21
2	149	50	13.88	29.01	2.43	438.90	52.44	8.57	80.76
3	137	50	16.92	14.48	2.24	405.14	70.68	4.18	55.82
4	124	50	12.92	14.81	1.75	376.19	50.30	3.40	49.36
5	124	62	11.79	16.27	1.78	369.40	47.19	3.49	45.89
6	137	62	10.83	14.24	1.81	328.25	49.28	2.05	42.15
7	148	59	15.88	34.47	2.30	420.58	54.93	8.28	72.46
8	133	73	12.59	13.93	1.85	323.48	58.14	1.99	44.49
9	124	75	13.26	20.23	2.05	441.71	47.36	6.03	58.96
10	124	88	17.16	38.66	2.90	571.80	64.23	9.47	90.13
11	122	94	15.32	27.25	2.37	439.37	57.65	6.45	71.96
12	111	100	16.73	15.27	2.11	456.78	73.08	1.72	53.89
13	124	38	10.10	12.07	1.65	274.24	41.27	2.32	43.56
14	136	36	10.62	12.52	1.64	308.04	40.47	4.34	45.78
15	149	37	12.96	19.27	2.05	323.00	44.71	4.29	59.34
16	162	37	11.01	14.78	1.92	305.25	41.29	5.09	56.66
17	151	26	11.01	20.03	1.88	318.38	41.74	3.84	57.27
18	162	25	12.22	13.22	1.92	255.57	39.86	6.16	51.00
19	174	37	13.36	11.39	1.83	297.27	38.96	1.64	55.82
20	175	25	12.41	17.36	2.11	248.18	41.31	2.31	60.87
21	162	12	10.26	8.68	1.58	240.43	40.61	2.45	45.29
22	131	28	11.16	12.65	1.62	286.18	40.89	3.49	42.85
23	125	24	12.04	12.26	1.64	312.84	47.04	2.27	43.59
24	108	40	13.45	12.73	1.93	379.43	60.18	1.94	48.05
25	97	38	12.46	12.07	1.70	316.14	50.93	2.24	43.59
26	86	46	12.41	11.48	1.77	317.31	49.16	2.40	43.75
27	72	65	18.43	12.43	2.35	432.63	98.70	0.0	54.18
28	76	77	13.14	12.00	1.98	356.95	61.40	0.0	47.25
29	86	75	14.00	10.93	2.14	368.83	62.10	0.0	52.04
30	86	91	14.36	20.07	2.27	423.72	56.05	2.00	65.05
31	98	87	15.39	12.49	2.06	454.27	73.71	0.0	53.66
32	99	73	11.98	12.71	1.69	406.31	43.11	0.0	48.04
33	99	64	13.41	14.68	1.89	375.17	56.80	1.04	47.28
34	102	49	10.29	11.56	1.39	322.10	42.29	1.48	38.98
35	111	49	12.66	11.41	1.79	349.29	58.83	2.06	46.16
36	111	62	12.08	14.29	1.81	340.92	47.52	3.59	49.36
37	114	77	19.09	38.02	2.93	519.68	70.95	7.41	92.92
38	110	87	13.33	14.98	1.70	498.42	52.81	4.19	54.37
39	121	156	16.64	42.90	2.73	439.30	59.94	17.53	105.87
40	123	145	14.00	26.59	2.22	417.45	49.45	9.19	75.80
41	125	131	13.96	14.76	1.69	363.61	41.49	5.40	57.91
42	124	117	13.69	27.57	2.15	394.05	45.49	7.59	75.28
43	111	125	11.03	11.79	1.34	362.14	28.22	4.81	45.04
44	112	137	13.00	11.86	1.65	329.15	40.00	5.35	51.52
45	111	149	13.88	14.90	1.65	408.98	47.22	5.63	54.03

46	111	162	10.72	12.90	1.40	286.12	39.98	2.84	45.33
47	111	175	13.02	14.27	1.75	330.82	39.19	9.79	56.38
48	118	183	14.47	73.05	2.44	285.25	43.38	41.22	109.24
49	90	209	11.13	15.20	1.70	383.35	33.62	4.94	49.56
50	99	198	12.05	14.25	1.89	287.42	34.74	8.11	51.94
51	112	191	12.65	30.77	2.31	308.60	36.46	15.94	74.17
52	99	174	12.98	14.84	1.81	297.15	33.04	10.06	53.55
53	99	160	13.47	12.92	1.95	305.14	45.45	4.08	49.66
54	99	150	12.36	13.65	1.68	303.29	36.02	5.34	48.29
55	99	137	12.50	13.11	1.73	265.80	35.07	2.14	46.04
56	99	124	12.60	12.40	1.89	320.32	42.50	2.48	49.13
57	96	116	14.94	12.50	2.00	371.41	48.12	3.13	51.37
58	74	100	13.31	16.20	1.83	360.82	37.62	5.42	50.34
59	86	162	12.69	13.72	1.64	295.56	32.28	8.47	47.65
60	87	174	14.34	14.36	1.94	487.24	41.76	4.94	53.77
61	83	182	11.82	12.31	1.69	272.91	36.56	5.23	47.37
62	86	198	12.56	13.62	1.77	278.88	35.07	4.58	47.72
63	99	186	14.32	16.05	1.84	423.29	36.15	5.49	51.55
64	81	166	15.72	16.60	2.06	552.00	43.91	7.34	55.82
65	79	153	13.47	13.04	1.79	367.69	39.69	8.34	47.90
66	83	116	15.01	12.51	2.04	319.20	52.78	2.71	49.42
67	92	131	12.65	11.28	1.78	287.90	43.00	3.70	45.34
68	89	138	11.91	12.45	1.59	257.82	35.79	3.89	45.06
69	87	150	12.58	12.11	1.68	267.69	42.20	4.01	46.09

SERIES D INTERTIDAL SAMPLES (MAY 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN
1	174	37	13.55	10.04	1.80	265.22	35.86	3.39	51.82
2	174	25	12.93	15.33	2.03	243.51	40.99	4.79	56.88
3	162	37	11.27	12.97	1.93	272.78	37.85	7.77	51.47
4	159	49	13.98	26.49	2.73	305.42	45.04	6.22	75.23
5	149	50	15.05	25.11	2.46	456.00	52.42	5.75	68.76
6	148	59	13.79	17.88	1.93	356.67	56.35	3.02	48.24
7	137	62	14.58	31.01	2.26	461.15	49.07	4.07	66.19
8	136	50	16.92	32.79	2.72	467.22	53.53	4.97	75.80
9	149	38	12.32	14.28	1.87	289.55	37.30	3.10	51.90
10	151	26	13.48	24.21	2.20	384.29	41.05	1.02	62.18
11	161	25	10.57	11.40	1.86	230.87	31.47	3.54	47.44
12	161	12	13.32	9.57	1.79	257.03	46.87	2.57	46.19
13	180	12	12.43	17.06	2.40	245.23	43.26	5.61	62.80
14	181	7	8.72	7.33	1.34	182.62	28.80	4.20	35.10
15	123	24	13.88	13.72	1.93	312.34	46.77	1.93	48.21
16	98	37	16.76	12.89	2.26	377.71	62.06	1.14	48.52
17	86	46	13.52	13.67	1.60	294.28	35.97	4.81	44.29
18	86	62	15.69	28.39	2.35	425.05	46.63	4.24	66.38
19	86	75	15.87	17.31	2.07	416.18	57.57	0.77	52.39
20	72	76	18.87	41.75	2.99	528.28	56.88	5.14	83.17
21	86	88	14.34	14.90	1.69	302.46	44.59	3.07	43.79
22	99	73	16.29	20.79	2.13	430.24	51.35	5.61	57.10
23	98	62	16.89	18.96	1.99	581.70	50.44	2.14	54.71
24	99	50	18.62	23.58	2.04	771.67	55.53	4.16	58.81
25	111	37	14.56	15.00	1.71	341.79	44.07	3.41	46.90
26	123	37	14.00	13.33	1.73	327.51	44.01	1.52	43.96
27	131	27	15.00	14.76	1.82	304.30	44.82	7.19	47.67
28	136	37	15.43	19.59	2.13	373.21	45.74	5.70	56.88
29	123	50	17.21	16.06	2.34	426.12	63.68	3.49	54.93
30	111	50	16.14	14.34	2.09	382.06	53.88	4.83	50.49

31	110	62	17.51	13.26	2.29	379.77	67.13	2.66	51.10
32	98	87	20.41	35.70	2.69	712.31	60.00	7.70	79.78
33	111	190	15.94	38.34	2.73	358.28	48.97	16.51	85.71
34	97	185	13.05	14.27	1.77	309.12	39.30	9.02	50.92
35	98	174	13.22	14.39	1.92	332.84	41.45	5.95	52.17
36	117	183	16.39	86.68	2.97	337.95	51.71	50.69	126.49
37	111	174	18.79	20.55	2.24	356.58	44.47	14.81	65.60
38	99	160	15.60	13.26	2.12	322.22	44.68	4.52	51.52
39	86	161	21.84	25.40	2.06	1016.71	54.78	7.54	64.52
40	80	155	15.43	12.84	1.78	293.29	42.10	4.43	47.14
41	86	149	15.41	13.14	1.87	334.11	46.29	7.25	47.42
42	86	137	14.10	13.08	1.87	369.74	55.80	4.10	48.78
43	86	124	15.33	14.55	2.03	491.73	57.93	4.13	50.67
44	81	115	14.14	14.10	1.97	397.94	55.01	3.91	50.35
45	74	100	13.39	17.04	1.92	379.84	48.70	2.51	54.26
46	87	174	12.22	13.92	1.96	357.51	44.88	5.50	53.52
47	82	181	14.66	14.33	1.84	532.73	52.99	4.43	54.29
48	86	197	12.71	13.20	1.77	274.22	44.89	4.95	49.41
49	89	209	10.05	13.76	1.68	531.46	39.80	2.82	46.50
50	99	197	11.02	13.38	1.66	295.76	38.58	7.23	48.89
51	111	100	10.63	14.80	1.66	447.38	45.27	3.12	44.64
52	110	87	13.52	33.60	2.64	454.34	53.53	7.30	72.63
53	112	77	13.54	30.82	2.63	441.47	51.79	6.62	71.92
54	124	62	11.18	13.60	1.82	292.13	49.59	3.80	41.16
55	131	69	16.48	44.35	3.14	575.62	61.30	9.52	87.68
56	124	75	12.82	18.05	2.01	505.08	48.23	4.02	56.39
57	124	87	14.70	40.37	2.78	548.20	57.41	9.39	80.19
58	121	94	10.51	21.75	2.05	383.05	44.72	5.41	55.64
59	96	116	10.38	13.48	1.83	376.51	47.67	4.58	50.07
60	99	123	13.88	12.27	2.27	480.09	62.24	4.10	52.17
61	98	13	10.14	11.59	1.58	321.59	37.56	4.76	46.70
62	98	149	10.63	11.80	1.66	321.72	41.40	3.88	45.57
63	111	161	9.25	12.80	1.51	252.75	38.07	4.10	41.94
64	111	149	12.90	20.31	2.23	339.91	44.56	8.01	63.49
65	111	136	11.03	15.62	1.82	344.99	42.61	7.31	52.78
66	111	124	9.81	10.04	1.26	292.18	29.50	4.37	37.93
67	123	117	14.84	30.51	2.49	292.18	51.88	7.02	75.87
68	124	131	13.04	29.76	2.37	344.99	45.70	9.07	73.40
69	122	144	16.15	37.95	2.88	443.56	56.98	14.80	90.72
70	121	155	13.07	34.97	2.53	369.63	48.02	12.83	80.00

SERIES E INTERTIDAL SAMPLES (JUNE 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN
1	118	183	16.04	72.60	3.19	389.59	57.14	35.84	120.29
2	111	174	12.20	14.63	1.92	296.58	39.83	9.97	57.92
3	99	174	11.12	11.79	1.61	274.33	35.12	6.22	45.66
4	87	174	11.50	12.12	1.80	260.79	41.29	4.74	49.49
5	86	161	11.07	10.97	1.92	279.81	46.58	2.31	46.56
6	102	162	10.21	11.32	1.69	267.48	42.63	3.23	44.26
7	111	161	11.22	12.65	1.78	350.35	42.85	5.23	50.45
8	121	155	12.80	30.37	2.58	408.79	46.96	15.60	83.41
9	111	149	10.59	11.46	1.70	357.90	38.10	6.67	51.29
10	98	149	11.09	14.91	1.91	317.54	42.55	4.13	54.26
11	86	149	12.58	12.90	1.98	355.16	51.83	4.53	50.68
12	86	137	13.18	16.33	1.89	690.05	51.41	6.54	55.19
13	86	124	12.88	12.40	1.89	351.65	54.00	4.15	48.19
14	94	115	10.86	10.15	1.66	306.38	39.54	6.17	45.32

15	99	123	9.41	11.09	1.34	208.64	37.83	2.56	41.19
16	98	137	8.99	10.76	1.68	222.28	35.24	4.45	42.13
17	111	137	10.44	11.27	1.80	319.53	38.63	7.00	49.22
18	123	144	11.50	13.07	1.81	268.07	35.36	6.40	53.52
19	121	130	10.88	13.62	1.89	342.09	37.68	8.27	55.35
20	121	103	12.64	24.68	2.49	438.76	44.33	8.07	72.53
21	111	124	11.19	14.30	1.54	298.83	39.89	4.45	41.83
22	111	190	9.16	15.74	1.81	234.47	35.87	9.05	52.43
23	99	198	11.34	11.92	1.88	262.92	41.20	4.82	46.79
24	97	184	11.15	13.88	1.69	492.17	37.60	8.92	50.43
25	111	100	9.62	20.22	1.85	332.68	47.64	2.88	48.15
26	111	87	14.84	22.60	2.16	453.06	53.24	4.69	55.87
27	98	86	16.91	25.71	2.22	604.76	52.84	4.27	61.25
28	86	87	9.90	15.67	1.65	277.85	37.47	2.21	42.08
29	87	75	13.46	12.95	1.95	361.09	52.51	2.43	46.50
30	72	77	14.28	14.49	2.03	392.11	62.29	0.79	46.90
31	85	46	10.87	13.14	1.75	310.63	42.26	2.89	44.72
32	98	37	13.89	12.62	2.03	343.00	61.93	1.64	43.74
33	99	50	13.95	30.70	2.44	360.03	50.13	3.28	71.03
34	98	62	10.72	15.55	1.79	287.06	42.77	1.75	46.79
35	86	62	12.85	13.16	2.00	370.42	53.91	1.23	50.39
36	96	74	12.64	26.76	2.18	416.89	46.96	5.53	60.87
37	114	76	13.33	15.35	1.98	527.79	57.21	3.41	51.61
38	110	62	14.34	23.18	2.26	435.29	59.40	4.86	59.87
39	111	49	11.49	11.66	1.75	330.37	48.79	3.06	43.05
40	111	37	9.79	12.77	1.67	286.21	41.60	3.75	43.09
41	123	24	10.60	13.35	1.63	268.59	37.95	4.17	42.75
42	136	25	11.03	15.10	1.88	264.75	40.24	6.56	49.58
43	151	26	13.10	26.62	2.32	301.65	46.59	7.52	69.19
44	123	37	10.66	13.63	1.66	317.25	41.28	2.62	41.95
45	136	36	10.90	12.92	1.65	279.59	36.00	5.12	42.60
46	149	37	11.28	14.85	1.75	262.25	37.38	6.39	47.75
47	162	37	10.04	12.84	1.78	343.40	34.65	3.64	44.76
48	159	49	12.38	26.61	2.51	279.23	45.40	6.26	67.29
49	122	94	16.85	42.04	3.15	629.50	60.14	9.93	87.51
50	124	87	10.32	15.12	1.75	281.54	42.51	0.92	40.13
51	132	69	13.20	29.40	2.26	417.38	46.51	3.97	63.02
52	136	62	11.31	23.12	1.95	350.48	44.76	3.62	51.03
53	148	59	15.12	38.57	2.87	577.47	56.91	6.98	78.81
54	149	50	11.80	24.66	2.47	326.43	45.53	4.74	68.83
55	136	50	10.47	13.27	1.69	370.07	43.99	0.47	45.21
56	161	25	9.87	12.05	2.03	242.89	38.50	3.38	51.48
57	174	37	11.03	12.53	2.01	225.09	36.12	3.86	58.77
58	174	24	10.47	13.40	1.85	205.96	36.20	3.04	53.06
59	164	12	10.69	8.90	1.89	248.98	42.34	1.83	49.46
60	180	12	7.78	8.73	1.56	174.07	28.35	3.18	47.83
61	181	7	7.04	7.95	1.38	166.43	27.88	1.58	40.60
62	124	50	9.08	16.00	1.74	253.46	44.65	0.0	41.23
63	124	62	7.44	15.62	1.42	256.98	37.08	0.0	37.93
64	124	75	11.80	22.32	1.82	408.36	43.15	0.0	49.48

SERIES F INTERTIDAL SAMPLES (OCTOBER 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN
1	159	48	15.69	36.75	2.93	315.15	55.33	12.76	79.25
2	148	49	14.19	24.50	2.15	262.62	49.49	7.59	56.76
3	136	50	12.20	12.97	1.41	424.24	42.52	0.0	42.83
4	125	49	12.55	11.53	1.52	290.90	49.90	0.0	39.62



5	112	49	12.20	11.89	1.64	307.07	49.62	0.0	44.98
6	107	74	12.73	11.53	1.48	375.75	38.89	8.30	44.98
7	111	88	12.84	16.57	1.96	371.71	44.98	0.0	50.33
8	111	100	10.60	12.25	1.64	270.70	43.23	0.0	46.05
9	124	74	12.20	13.33	1.68	331.31	38.31	0.0	46.05
10	124	61	16.23	10.81	1.84	375.75	55.56	0.0	49.26
11	149	37	9.93	7.92	1.56	202.02	34.80	0.0	46.05
12	168	30	12.13	13.69	1.96	270.70	45.02	0.0	53.54
13	117	156	12.66	16.21	2.03	307.07	44.49	13.21	55.68
14	117	145	12.45	14.41	1.72	274.74	38.44	7.23	49.26
15	118	132	13.66	23.42	2.19	347.47	46.42	10.70	66.39
16	118	121	13.44	23.06	2.27	404.04	42.48	0.0	63.18
17	111	123	9.05	10.81	1.64	234.34	35.59	3.54	41.76
18	111	135	10.25	10.09	1.64	294.94	35.85	6.63	47.12
19	112	150	11.14	10.81	1.76	307.07	39.11	3.70	46.05
20	112	162	11.63	10.45	1.76	262.62	37.21	5.06	49.26
21	88	175	15.52	11.53	2.23	379.79	52.90	3.42	53.54
22	85	162	12.89	14.96	1.64	361.00	40.67	4.36	47.27
23	80	167	24.48	32.78	1.88	1922.74	67.62	6.45	71.43
24	79	153	10.52	11.40	1.48	235.43	41.20	1.24	42.02
25	86	150	12.02	12.11	1.52	294.29	40.62	0.0	45.17
26	86	138	10.97	11.40	1.56	266.83	42.83	0.0	44.12
27	86	124	10.80	9.26	1.56	235.43	40.18	0.0	40.97
28	83	117	15.04	10.63	1.84	282.52	54.81	0.0	46.22
29	99	175	11.91	8.90	1.37	255.05	35.80	0.0	40.97
30	99	161	11.70	9.62	1.48	274.67	43.05	0.0	40.97
31	99	150	11.25	9.97	1.41	266.83	39.30	0.0	42.02
32	99	138	10.93	10.33	1.41	255.05	37.37	0.0	42.02
33	99	124	10.73	10.33	1.37	251.13	35.15	0.0	40.97
34	95	116	11.95	9.26	1.64	282.52	47.83	0.0	43.07
35	74	100	13.95	11.40	1.84	313.91	56.45	0.0	48.32
36	72	76	12.37	11.40	1.76	302.14	52.48	0.0	44.12
37	86	75	13.95	10.69	1.80	333.53	54.90	0.0	45.17
38	99	72	11.32	16.74	1.76	443.40	40.98	0.0	49.37
39	99	64	10.83	12.47	1.64	282.52	43.72	0.0	42.02
40	100	50	11.00	13.89	1.72	333.53	42.61	0.0	46.22
41	111	37	9.65	11.75	1.48	266.83	38.51	0.0	42.02
42	123	37	12.47	14.25	1.92	282.52	44.17	0.0	49.37
43	137	37	9.89	12.90	1.52	263.12	34.77	0.0	39.73
44	152	27	8.43	10.03	1.32	247.64	29.85	0.0	36.60
45	99	87	11.20	15.40	1.76	355.98	42.92	0.0	43.92
46	86	87	11.50	11.46	1.93	282.46	56.90	0.0	41.83

SERIES G FORE-SLOPE SAMPLES (OCTOBER-NOVEMBER 1974)

STN	E	N	CO	CU	FE	MN	NI	PB	ZN
1	61	94	11.50	30.81	2.29	290.20	43.85	0.0	66.92
6	61	100	12.22	31.53	2.33	309.55	46.19	0.0	67.97
7	64	100	9.99	15.76	2.01	259.25	48.73	0.0	44.96
20	67	113	14.10	39.41	3.05	355.98	51.42	7.49	87.84
21	70	113	14.07	37.62	2.93	355.98	49.13	12.14	83.66
22	73	113	13.08	33.68	2.73	317.29	50.03	0.0	73.20
30	70	126	13.57	37.98	2.89	340.50	51.60	5.49	86.79
31	73	126	10.19	12.54	2.01	247.64	40.95	0.0	43.92
39	70	138	14.63	40.13	2.81	297.94	50.84	8.79	86.79
40	73	138	9.08	10.75	1.40	212.81	36.37	0.0	39.73
55	61	163	13.08	40.13	3.01	321.16	50.57	13.66	92.02
56	67	163	9.96	32.25	2.49	278.59	45.75	8.13	71.11

57	70	163	11.20	31.53	2.41	278.59	44.51	10.21	71.11
58	73	163	9.14	11.82	1.88	247.64	45.57	0.0	43.92
64	61	176	14.23	43.00	3.05	317.29	50.52	13.90	92.02
65	67	176	13.57	38.70	3.01	321.16	52.82	8.20	87.84
66	70	176	12.09	35.11	2.61	278.59	50.61	9.69	77.38
67	73	176	9.88	9.08	1.40	190.45	30.95	0.0	38.71
72	49	188	13.75	41.04	3.19	376.93	50.25	14.91	101.07
73	61	188	13.27	42.86	3.19	333.29	54.59	12.99	96.77
74	67	188	15.89	43.58	3.11	349.16	54.28	16.39	98.92
75	70	188	13.03	34.50	2.60	293.61	45.96	9.76	80.64
76	73	188	12.62	30.14	2.53	269.80	45.49	5.41	70.96
77	80	188	9.75	11.62	1.63	218.22	35.82	4.01	43.01
82	49	200	14.72	49.03	3.03	329.32	47.41	35.47	133.33
83	61	200	15.82	45.76	3.19	357.09	52.72	16.19	103.22
84	67	200	14.40	45.40	3.19	365.03	54.90	14.28	98.92
85	73	200	11.42	33.78	2.60	301.55	48.44	7.97	79.57
86	80	200	9.37	11.62	1.83	226.16	39.78	0.0	45.16
91	61	213	13.27	43.58	2.92	333.29	52.89	13.94	101.07
92	67	213	14.13	44.31	3.11	333.29	50.60	11.88	100.00
93	73	213	11.79	33.41	2.45	269.80	43.71	11.52	75.26
94	76	213	10.91	26.15	2.21	249.96	41.05	2.53	64.51
95	80	213	11.52	18.16	2.41	257.90	49.13	0.0	55.91
96	80	219	10.56	22.52	2.14	253.93	41.42	0.0	59.14
97	76	219	11.90	22.52	2.14	249.96	42.44	0.0	60.21
98	73	219	11.83	30.87	2.41	269.80	42.23	0.0	73.11
99	67	219	14.44	45.76	3.11	333.29	49.82	11.65	98.92
104	86	232	10.63	18.01	1.57	205.68	35.95	0.0	51.20
105	86	238	14.52	40.36	2.67	304.57	52.71	13.48	88.53
106	80	232	9.54	15.49	1.53	217.55	38.20	0.0	44.80
107	73	232	11.92	30.27	2.28	261.06	44.50	12.05	72.53
108	67	232	13.65	40.36	2.95	308.52	50.77	14.35	90.66
109	80	238	13.65	34.23	2.51	276.88	45.80	8.91	74.66
117	73	244	11.72	31.71	2.36	268.97	45.58	6.79	78.93
118	80	244	11.82	30.99	2.28	261.06	42.69	11.95	74.66
119	86	244	11.72	26.30	2.32	253.15	42.77	7.98	73.60
120	92	250	12.32	34.95	2.55	268.97	47.14	12.82	78.93
123	73	250	12.78	41.80	2.95	344.12	50.51	15.82	98.13
124	67	250	13.82	51.89	3.14	403.46	49.32	37.39	109.86
126	67	257	14.38	58.37	2.99	316.44	52.58	59.25	109.86
130	92	257	12.32	43.24	2.67	292.70	48.89	15.13	91.73
131	92	263	14.22	52.97	3.14	332.26	51.78	22.50	104.53
132	86	263	12.98	54.05	2.99	324.35	51.91	25.39	106.66
133	162	6	8.81	15.13	1.69	193.82	39.39	0.0	44.80
134	155	6	8.65	9.73	1.77	253.15	47.45	0.0	40.53
135	155	12	11.09	14.41	2.04	229.41	50.24	3.67	53.33
136	148	6	10.56	10.81	1.85	245.24	47.10	0.0	42.66
137	143	12	14.12	10.09	2.36	268.97	67.88	0.0	42.66
138	143	12	17.90	34.51	2.95	324.00	54.90	6.08	79.37
139	143	18	13.67	12.75	2.24	236.33	47.07	0.0	45.95
140	136	18	13.54	19.50	2.44	240.14	41.77	0.0	55.97
141	136	12	11.89	13.13	2.63	243.95	50.33	0.0	46.78
142	136	6	15.54	20.63	3.30	289.69	53.05	0.0	66.84
143	130	6	9.86	11.25	2.16	217.27	39.01	0.0	40.10
144	130	12	9.86	10.12	2.51	278.26	52.96	0.0	48.46
145	130	18	13.45	32.26	2.95	339.24	46.72	0.0	72.68
149	117	6	10.21	11.25	2.44	274.44	50.20	0.0	50.13
150	117	12	12.15	15.00	2.67	304.94	56.98	0.0	55.97
151	117	18	10.08	48.76	2.48	289.69	51.34	0.0	55.97
152	111	18	7.08	10.12	2.04	259.20	46.11	0.0	41.77
153	111	12	17.20	24.76	2.99	285.88	54.68	0.0	73.52

154	111	6	14.76	25.13	3.07	289.69	55.56	0.0	75.19
156	98	12	13.67	23.25	2.59	251.57	44.95	4.67	68.51
157	86	12	10.77	18.75	2.28	221.08	37.82	0.0	55.14
159	98	18	11.63	10.50	2.04	247.76	45.42	0.0	39.26
161	110	24	15.24	20.25	2.67	312.56	52.34	0.0	60.15
163	105	24	14.19	26.26	2.83	289.69	48.76	0.0	62.66
165	98	31	13.45	25.88	2.51	274.44	47.67	0.0	60.99
166	98	24	12.63	12.00	2.08	274.44	40.71	0.0	43.44
167	92	24	9.12	11.92	1.63	203.79	36.23	0.0	40.44
168	86	24	7.14	13.79	1.94	221.67	40.96	0.0	48.02
171	80	31	9.53	17.51	2.02	228.82	38.70	0.0	53.08
172	86	31	7.37	11.92	1.67	207.37	37.93	0.0	37.91
173	92	31	9.61	13.41	1.94	228.82	46.10	0.0	45.49
174	95	31	9.23	19.75	2.06	232.40	41.95	0.0	48.02
175	92	37	8.49	12.30	1.94	264.58	49.46	0.0	42.12
176	89	37	9.87	15.65	1.86	221.67	41.35	0.0	42.12
177	86	37	9.76	19.38	2.06	228.82	41.52	0.0	48.02
178	80	37	9.08	19.75	2.25	239.55	43.59	0.0	52.23
179	73	37	10.40	26.83	2.53	261.00	43.07	4.61	65.71
180	67	37	9.68	24.22	2.45	257.43	38.91	4.73	64.87
181	61	37	8.37	20.87	2.18	225.25	37.12	8.48	63.19
182	67	44	10.40	22.36	2.10	225.25	44.80	6.43	58.13
183	73	44	10.13	24.97	2.02	214.52	45.10	4.63	52.23
184	80	44	13.00	27.95	2.33	264.58	47.45	7.60	62.34
185	83	44	9.05	14.91	1.86	225.25	43.46	5.06	45.49
186	86	44	9.72	16.02	1.86	221.67	44.45	4.11	43.81
187	80	50	13.75	36.52	2.72	314.63	51.83	6.49	71.61
188	77	50	11.67	30.56	2.45	275.30	50.07	5.81	62.34
189	73	50	11.67	26.09	2.29	261.00	49.46	4.73	60.66
190	67	50	14.34	24.22	2.07	241.77	43.87	6.35	55.83
191	61	50	11.73	30.56	2.47	270.22	44.26	8.88	66.66
192	54	50	12.28	30.56	2.63	295.11	40.54	10.66	73.33
194	54	56	12.69	29.32	2.39	266.66	43.08	12.42	62.50
195	61	56	11.63	29.07	2.39	277.33	52.26	7.45	62.50
196	67	56	13.06	30.56	2.55	291.55	48.20	9.53	65.83
197	70	56	12.50	27.95	2.31	277.33	49.89	3.20	58.33
198	73	56	13.31	38.39	2.87	334.22	55.10	12.77	72.50
199	67	62	11.88	25.34	2.23	291.55	49.62	4.71	54.16
200	64	62	11.70	28.32	2.47	291.55	47.44	0.0	61.66
201	61	62	12.58	27.95	2.35	280.88	42.38	0.0	56.66
202	54	62	12.98	29.07	2.47	284.44	42.11	7.80	62.50
203	48	62	10.13	25.34	1.99	248.88	41.59	0.0	60.00
204	48	68	12.80	26.83	1.95	227.55	41.68	0.0	56.66
205	54	68	12.69	26.09	2.23	270.22	44.75	0.0	68.33
206	61	68	12.54	27.95	2.19	277.33	43.60	0.0	61.66
207	64	68	10.97	20.50	1.83	248.88	42.11	0.0	51.66
208	61	75	10.31	13.79	1.75	266.66	43.82	0.0	40.83
209	57	75	12.98	28.70	2.27	291.55	44.04	4.47	66.66
210	54	75	12.76	30.56	2.39	291.55	46.69	0.0	66.66
211	48	75	12.87	30.56	2.31	284.44	43.34	0.0	66.66
212	36	75	13.11	25.32	2.09	245.87	45.40	7.59	60.65
213	36	88	12.86	30.09	2.29	274.80	46.09	8.87	67.21
214	48	88	11.25	29.35	2.21	274.80	46.00	5.49	62.29
215	48	81	12.05	30.09	2.25	274.80	47.77	6.93	65.57
216	54	81	12.09	29.35	2.21	278.41	47.08	6.83	62.29
217	57	81	11.14	26.42	2.17	274.80	49.07	6.31	59.83
218	61	81	9.36	19.08	1.70	242.26	40.78	0.0	39.34
219	54	88	11.91	34.12	2.57	318.19	51.16	6.68	68.85
220	61	88	10.65	24.58	2.05	249.49	48.81	8.68	59.01

TRACE METAL VALUES IN PPM; FE IN %

PB VALUES BELOW DETECTION LIMIT WHERE LISTED AS 0.0

## APPENDIX B

## FIRST PARTIAL EXTRACTION EXPERIMENT RESULTS

FIRST COLUMN LISTED UNDER EACH ELEMENT REPRESENTS METAL EXTRACTED IN  
1.0 M HYDROXYLAMINE HYDROCHLORIDE AND 25% ACETIC ACID

SECOND COLUMN REPRESENTS METAL EXTRACTED IN SUBSEQUENT 4:1 NITRIC:PERCHLORIC  
ACID ATTACK

ALL SAMPLES PREVIOUSLY LEACHED WITH 1 M MAGNESIUM CHLORIDE

ALL VALUES IN PPM EXCEPT FE IN %

#	ZN		CU		PB		CO		NI		FE		MN	
SERIES A INTERTIDAL SAMPLES (FEBRUARY 1974)														
3	7.3	54.8	4.6	22.8	3.1	0.0	2.3	10.3	4.6	33.3	.27	2.30	92.9	198.4
4	7.9	46.7	3.6	18.0	2.7	0.0	2.5	8.7	4.4	32.1	.20	2.22	37.4	187.5
12	8.3	40.2	2.6	10.0	3.2	0.0	2.5	8.0	3.7	26.7	.23	1.74	111.8	158.9
13	10.0	44.0	2.4	10.2	3.0	0.0	2.3	11.8	3.0	49.6	.24	2.25	42.3	232.6
18	5.9	40.0	0.8	9.0	2.1	0.0	1.7	11.3	3.1	52.9	.12	2.10	9.8	239.4
20	9.6	37.8	2.4	12.0	2.4	0.0	2.2	9.2	3.3	28.0	.23	1.85	34.9	169.9
21	8.9	40.2	1.8	10.0	1.8	0.0	2.7	8.5	3.1	29.9	.19	1.81	28.2	169.9
22	11.6	60.4	4.4	23.6	4.5	0.0	2.4	11.0	4.1	38.2	.26	2.44	36.1	209.4
23	11.9	68.6	5.4	31.7	5.4	0.0	3.1	13.2	4.7	39.2	.33	2.91	97.9	243.8
26	9.3	65.3	5.4	26.3	5.3	2.3	2.6	11.8	5.5	41.3	.30	2.84	91.6	228.0
32	8.6	50.6	3.6	20.2	4.6	1.9	3.2	11.1	5.1	40.4	.24	2.28	65.4	193.9
34	6.8	39.1	2.6	9.0	2.2	0.0	3.7	11.9	4.3	43.9	.14	1.95	75.3	209.8
39	5.8	31.4	2.6	7.6	1.5	0.0	2.4	7.2	3.2	31.1	.12	1.66	43.0	183.0
40	9.5	37.5	3.5	8.6	4.5	0.0	5.3	11.5	4.3	41.1	.16	1.88	69.8	187.5
50	9.2	47.5	3.6	16.4	4.5	0.0	2.1	7.9	2.6	30.7	.20	2.07	55.8	175.8
51	10.2	48.1	3.6	15.6	2.5	0.0	2.8	12.1	3.3	33.9	.27	2.06	57.5	183.0
52	9.7	45.7	3.4	14.0	5.6	0.0	2.2	11.0	2.9	30.0	.22	2.03	57.5	175.8
53	11.0	48.1	3.6	16.7	7.3	0.7	3.1	11.6	3.8	31.8	.23	1.92	75.3	164.4
54	22.0	41.6	15.8	31.7	49.7	9.0	1.8	10.9	3.0	28.2	.21	1.70	8.8	150.8
55	26.1	62.8	11.2	34.0	22.3	3.0	3.5	12.8	4.2	37.8	.34	2.43	64.2	216.6
59	11.5	43.2	3.0	12.9	5.6	0.0	3.6	14.1	4.4	33.3	.24	1.81	134.3	157.6
SERIES B FORE-SLOPE SAMPLES (MARCH 1974)														
19	22.0	67.7	3.2	32.1	13.7	10.1	3.1	13.0	4.4	42.7	.34	2.65	106.7	221.2
25	4.1	35.4	2.6	95.8	0.4	0.0	2.3	9.7	3.5	41.3	.13	1.92	39.7	216.0
32	12.9	57.1	3.8	22.9	7.1	0.0	3.1	11.5	4.0	39.2	.30	2.32	52.0	203.0
40	10.8	47.5	3.6	18.4	4.9	0.9	2.5	10.7	3.6	30.7	.24	2.07	40.4	180.8
52	14.9	74.1	4.4	38.1	8.8	5.2	2.5	11.6	4.2	41.2	.18	3.00	53.6	251.2
66	14.7	68.5	4.6	34.1	9.6	0.0	2.4	11.6	4.0	37.0	.26	2.63	58.2	238.6
72	18.4	78.1	2.8	41.7	10.1	5.8	1.4	12.6	3.3	40.0	.38	3.00	123.0	253.4
88	9.3	37.0	2.8	12.4	3.4	0.0	2.1	10.5	3.1	28.9	.18	1.92	23.7	178.7
98	15.0	62.8	4.4	31.7	7.6	2.6	2.3	10.7	3.5	35.4	.24	2.50	48.5	220.4
109	11.8	49.9	3.2	17.6	5.0	0.0	1.8	8.2	3.6	25.7	.11	1.70	44.6	167.6
119	15.1	59.6	4.6	25.9	9.4	3.5	2.9	14.0	3.4	34.4	.29	2.29	46.7	198.5
131	23.6	84.1	6.4	51.7	16.6	6.7	3.0	14.6	4.1	42.1	.41	3.13	69.0	268.8
132	24.7	86.5	6.2	55.2	19.7	11.2	2.4	14.4	4.4	44.7	.38	3.20	57.5	275.6
144	6.0	38.3	2.4	11.3	2.4	0.0	2.5	11.4	3.6	37.7	.20	1.81	34.7	178.1
160	4.5	35.4	1.4	8.4	0.8	0.0	1.8	9.6	2.7	34.3	.12	1.70	21.1	205.0
186	9.3	46.5	4.0	15.9	3.5	0.0	2.8	11.7	4.9	39.3	.28	2.29	57.9	203.0
214	13.5	58.8	2.6	27.9	7.3	0.0	2.7	12.5	3.7	37.8	.24	2.47	69.0	203.0

## APPENDIX C

CO, CU, FE(%), MN, NI, PB AND ZN CONTENT (PPM) OF SEDIMENT CORES  
FROM INTERTIDAL REGIONS OF THE FRASER DELTA-FRONT

DEPTHS MEASURED IN CM

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
9	1. 6.	10.46	15.66	1.82	185.46	35.90	4.63	55.45		
9	6. 11.	9.54	16.56	1.80	201.73	34.51	5.57	55.45		
9	11. 16.	12.15	18.80	1.93	211.49	35.58	4.06	59.03		
9	16. 21.	10.67	17.90	1.88	204.98	38.38	4.22	56.34		
9	21. 26.	12.31	17.46	1.90	204.98	37.54	4.10	56.34		
9	26. 31.	11.89	19.69	1.93	211.49	40.35	6.28	58.13		
9	31. 36.	14.60	25.06	2.27	240.77	44.12	7.27	65.29		
9	36. 41.	12.27	23.27	2.11	224.50	42.56	6.30	63.50		
9	41. 46.	12.70	22.38	2.11	234.27	40.82	3.73	57.24		
9	46. 51.	13.75	27.75	2.27	247.28	42.47	4.97	64.39		
9	51. 56.	17.80	31.33	2.42	299.34	45.07	4.65	66.18		
9	56. 61.	14.98	27.75	2.27	292.83	43.65	3.30	62.60		
9	61. 66.	11.77	25.51	2.42	266.80	48.61	5.29	64.39		
9	66. 71.	10.84	19.24	2.03	211.49	41.43	2.73	58.13		
9	71. 76.	11.30	18.80	1.95	195.22	41.62	2.82	57.24		
9	76. 80.	10.59	19.24	2.03	195.22	43.89	3.28	57.24		
10	1. 6.	8.78	15.66	1.84	185.46	38.00	0.0	50.08		
10	6. 11.	11.85	17.01	1.91	195.22	41.29	4.56	55.45		
10	11. 16.	10.34	17.90	1.95	198.48	42.70	5.02	57.24		
10	16. 21.	11.47	18.80	1.95	201.73	42.61	3.96	55.45		
10	21. 26.	13.58	19.69	2.03	208.24	44.36	2.96	56.34		
10	26. 31.	12.22	21.03	2.39	238.17	40.51	2.96	57.93		
10	31. 36.	14.12	21.94	2.46	238.17	44.05	3.44	60.69		
10	36. 41.	14.29	16.00	2.10	197.34	38.18	0.0	57.01		
10	41. 46.	13.40	18.29	2.21	207.55	41.91	3.16	57.93		
10	46. 51.	13.57	18.29	2.21	204.15	40.56	4.12	57.01		
10	51. 56.	10.02	17.37	2.28	210.95	38.72	2.05	55.17		
10	56. 63.	10.74	19.20	2.39	214.35	39.84	2.05	55.17		
11	0. 1.	12.26	28.34	2.60	279.00	44.09	12.02	68.96		
11	1. 6.	10.19	28.80	2.67	251.78	42.19	12.58	72.64		
11	6. 11.	10.31	29.71	2.81	258.59	45.73	11.80	72.64		
11	11. 16.	11.71	24.69	2.91	258.59	45.27	5.64	64.37		
11	16. 21.	9.31	17.83	2.63	238.17	43.50	5.97	52.41		
11	21. 26.	12.34	11.43	1.93	200.74	33.23	5.60	45.98		
11	26. 31.	12.09	10.97	1.90	193.94	34.92	3.42	44.14		
11	31. 36.	9.77	11.89	1.90	204.15	33.15	3.14	44.14		
11	36. 41.	10.65	12.34	1.93	204.15	34.34	1.51	44.14		
11	41. 46.	9.73	12.34	1.97	190.54	32.30	2.90	45.06		
11	46. 51.	10.31	13.71	1.93	193.94	34.70	3.03	45.98		
11	51. 56.	10.19	14.63	1.97	190.54	33.23	4.62	45.98		
11	56. 61.	8.09	13.71	1.97	197.34	36.12	3.94	47.82		
11	61. 66.	12.55	22.40	2.32	244.98	39.26	4.25	57.93		
11	66. 71.	13.05	22.99	2.44	248.38	44.68	5.44	55.02		
11	71. 76.	9.85	19.31	2.22	217.76	43.27	4.80	47.92		
11	76. 82.	9.93	14.71	2.04	200.74	40.01	2.64	44.37		

12	0.	1.	9.69	14.71	1.86	272.20	37.65	2.34	46.15
12	1.	6.	13.92	38.16	3.01	381.07	52.15	7.08	74.54
12	6.	11.	9.97	23.91	2.22	285.80	44.68	5.21	56.79
12	11.	16.	8.79	17.01	1.97	244.98	41.87	4.52	46.15
12	16.	21.	11.41	22.99	2.29	289.21	43.13	5.21	55.02
12	21.	26.	11.49	18.39	2.22	258.59	43.69	5.08	49.70
12	26.	31.	11.49	16.55	2.58	272.20	49.39	4.16	55.91
12	31.	36.	12.43	17.01	2.65	255.18	47.97	3.58	56.79
12	36.	41.	13.38	16.55	2.40	238.17	48.21	6.05	51.47
12	41.	46.	14.95	28.51	2.69	302.82	54.88	7.49	75.43
12	46.	51.	12.68	17.47	2.22	248.38	46.56	4.13	56.79
12	51.	56.	12.43	17.01	2.15	244.98	48.21	5.87	55.02
12	56.	61.	13.59	17.47	2.15	248.38	45.90	6.07	53.24
12	61.	66.	14.04	17.93	2.22	251.78	46.79	5.12	65.67
12	66.	71.	16.61	22.07	2.33	279.00	42.67	4.91	60.34
12	71.	76.	15.57	19.31	2.33	279.00	48.45	3.36	57.68
12	76.	81.	14.54	18.39	2.36	292.61	47.74	5.57	56.79
12	81.	86.	17.32	20.69	2.44	285.80	46.56	4.97	58.57
12	86.	91.	12.52	19.12	2.52	260.83	46.03	4.70	56.88
12	91.	96.	15.40	20.48	2.71	270.28	46.31	5.00	57.79
12	96.	101.	14.66	20.03	2.79	286.28	47.78	3.59	60.50
12	101.	106.	14.57	19.12	2.64	267.20	47.74	2.95	55.98
12	106.	113.	12.31	15.93	2.52	248.11	47.60	3.88	49.66

13	0.	1.	15.48	14.57	2.41	324.45	64.69	0.0	46.95
13	1.	6.	13.18	13.66	2.49	330.81	59.58	0.0	49.66
13	6.	11.	12.52	13.20	2.34	299.01	54.90	0.0	46.95
13	11.	16.	12.44	12.29	2.41	318.09	59.53	0.0	46.95
13	16.	21.	12.93	12.74	2.26	292.64	51.44	0.0	43.34
13	21.	26.	12.11	12.29	2.34	324.45	49.91	0.0	46.95
13	26.	31.	10.60	12.74	2.30	295.82	48.66	0.0	43.34
13	31.	36.	8.88	12.29	1.70	241.75	39.78	0.0	40.63
13	36.	41.	11.74	11.84	1.81	311.73	48.24	0.0	42.44
13	41.	46.	12.44	13.66	2.00	321.27	56.03	0.0	46.95
13	46.	51.	11.49	12.29	2.07	302.19	54.57	0.0	46.95
13	51.	56.	11.33	13.20	1.96	289.46	48.20	0.0	46.05
13	56.	61.	12.77	12.74	1.89	279.92	48.47	0.0	46.95
13	61.	66.	10.15	15.48	1.89	286.28	46.35	0.0	46.95
13	66.	71.	11.33	13.66	2.00	292.64	45.11	0.0	46.95
13	71.	76.	10.72	13.66	1.89	292.64	47.92	0.0	46.95
13	76.	81.	10.04	11.82	1.79	314.60	44.37	3.20	42.76
13	81.	86.	10.29	25.46	2.17	336.84	47.42	4.50	55.23

15	0.	1.	7.98	12.27	1.71	241.51	36.23	3.24	40.98
15	1.	6.	7.45	12.73	2.09	279.64	49.71	2.68	43.65
15	6.	11.	10.00	13.64	2.28	327.31	53.34	2.89	47.22
15	11.	16.	8.89	12.73	1.90	273.29	46.20	4.41	40.09
15	16.	21.	10.54	12.73	2.21	298.71	50.46	0.0	44.54
15	21.	26.	9.79	13.64	1.90	238.33	40.86	0.0	40.98
15	26.	31.	8.64	15.45	1.98	260.58	41.33	0.0	41.87
15	31.	36.	9.96	15.00	2.06	301.89	41.90	0.0	44.54
15	36.	41.	12.07	15.00	1.98	238.33	37.21	0.0	43.65
15	41.	46.	10.62	15.00	2.06	241.51	42.15	2.22	43.65
15	46.	51.	10.66	13.64	1.90	228.80	37.43	0.0	42.76
15	51.	56.	9.22	14.55	1.98	238.33	37.85	0.0	42.76
15	56.	64.	8.35	14.55	2.02	222.44	37.64	0.0	44.54

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
16	0. 1.	8.89	14.55	1.98	263.75	44.98	0.0	41.87	93.	0.5
16	1. 6.	12.28	13.64	2.44	217.78	61.66	0.0	48.11	96.	1.2
16	6. 11.	12.40	12.27	2.28	298.71	56.69	0.0	44.54	98.	1.6
16	11. 16.	11.62	13.64	2.28	305.06	59.08	0.0	48.11	99.	0.6
16	16. 21.	13.32	12.27	2.02	260.58	42.80	0.0	44.54	98.	1.0
16	21. 26.	11.86	13.64	2.09	241.51	43.45	0.0	42.76	98.	1.4
16	26. 31.	9.87	12.24	1.68	196.49	38.00	4.78	38.78	100.	1.4
16	31. 36.	11.97	16.83	2.23	242.10	50.05	0.0	47.21	79.	4.1
16	36. 41.	8.30	12.24	1.68	175.44	35.98	1.27	36.25	98.	1.3
16	41. 46.	10.19	13.77	1.88	217.54	37.05	0.0	37.93	97.	1.5
16	46. 51.	11.15	13.77	1.88	207.02	37.27	0.0	36.25	98.	1.1
16	51. 56.	8.69	13.39	1.74	182.46	36.71	0.0	35.41	97.	2.3
16	56. 61.	9.71	12.62	1.92	189.47	38.26	0.0	35.41	88.	1.9
16	61. 66.	9.14	13.39	1.81	171.93	39.51	0.0	34.56	97.	1.7
16	66. 70.	11.64	25.25	2.44	221.05	44.44	0.0	52.27	66.	2.6

18	0. 1.	7.83	14.15	1.92	224.56	36.54	0.0	33.72		
18	3. 8.	9.44	16.45	2.16	238.60	42.08	0.0	36.25		
18	8. 13.	11.24	15.30	2.16	252.63	45.62	0.0	37.09		
18	13. 18.	8.78	13.39	1.81	266.67	41.25	0.0	38.78		
18	18. 23.	8.96	14.54	1.68	256.14	35.55	0.0	37.93		
18	23. 28.	9.74	14.15	1.74	266.67	37.87	0.0	37.93		
18	28. 33.	8.63	16.07	1.71	259.65	39.56	0.0	38.78		
18	33. 38.	9.74	14.54	1.81	256.14	38.43	0.0	39.62		
18	38. 43.	8.99	16.07	1.74	221.05	37.83	0.0	37.09		
18	43. 48.	11.19	15.30	1.99	242.10	41.42	0.0	37.93		
18	48. 53.	9.14	18.74	1.68	217.54	33.20	0.0	38.78		
18	53. 58.	7.94	17.21	1.64	200.00	32.47	0.0	38.78		
18	58. 63.	8.00	15.42	1.71	212.53	32.36	0.0	37.80		
18	63. 67.	10.88	17.74	2.05	246.81	41.94	0.0	41.09		

19	0. 1.	9.31	17.74	1.91	263.95	39.17	0.0	39.45	99.	2.1
19	1. 6.	9.44	14.27	1.98	281.09	39.86	0.0	40.27	97.	2.0
19	6. 11.	9.18	15.04	2.05	284.52	38.90	0.0	38.62	89.	0.9
19	11. 16.	10.85	24.29	2.26	263.95	38.86	0.0	46.84	68.	1.0
19	16. 21.	8.64	23.90	2.19	253.67	38.78	0.0	47.66	82.	1.4
19	21. 26.	9.92	18.12	1.95	222.82	34.81	0.0	42.73	84.	2.0
19	26. 31.	8.42	21.59	2.12	239.96	35.92	0.0	45.20	81.	2.2
19	31. 36.	9.92	22.36	2.15	239.96	38.21	0.0	49.31	81.	1.5
19	36. 41.	11.76	25.45	2.46	260.52	42.29	0.0	51.77	69.	2.5
19	41. 46.	9.12	23.90	2.22	250.24	40.86	0.0	46.02	75.	1.9
19	46. 51.	9.53	21.59	1.85	277.67	38.78	0.0	43.55	80.	0.9
19	51. 56.	12.75	29.30	2.29	294.80	44.43	0.0	58.35	52.	1.2
19	56. 61.	9.12	20.82	1.91	267.38	38.05	0.0	46.84	85.	0.9
19	61. 66.	9.95	21.98	1.98	274.24	41.05	0.0	46.02	82.	1.8
19	66. 71.	10.17	23.90	2.19	294.80	39.63	0.0	52.59	70.	2.6
19	71. 76.	11.84	25.83	2.29	308.52	42.56	0.0	53.42	71.	2.8
19	76. 82.	7.08	14.65	1.61	229.67	31.94	0.0	34.51	99.	1.3

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
21	0. 1.	8.96	20.05	2.05	195.39	31.87	7.98	56.70		
21	1. 6.	11.46	25.06	2.15	205.68	35.27	9.79	61.63		
21	6. 11.	11.29	25.68	2.33	214.45	43.35	6.01	61.79		
21	11. 16.	11.02	21.40	1.99	201.05	38.36	3.96	54.38		
21	16. 21.	11.08	22.95	2.06	207.75	39.90	8.19	57.67		
21	21. 26.	9.74	22.18	2.06	207.75	39.17	6.68	57.67		
21	26. 31.	10.85	28.01	2.30	251.31	44.82	2.61	59.32		
21	31. 36.	10.90	26.07	2.37	227.85	42.52	0.0	59.32		
21	36. 41.	11.02	25.29	2.37	231.20	42.14	4.32	60.97		
21	41. 46.	11.93	25.68	2.40	227.85	42.14	4.26	57.67		
21	46. 51.	10.76	25.68	2.33	224.50	41.96	0.0	59.32		
21	51. 56.	11.52	28.40	2.57	241.26	43.35	0.0	62.62		
21	56. 61.	11.61	29.18	2.57	241.26	45.08	3.19	62.62		
21	61. 66.	13.17	27.23	2.54	231.20	43.48	4.92	60.14		
21	66. 71.	11.40	23.34	2.40	234.55	42.27	0.0	59.32		
21	71. 76.	12.78	24.51	2.40	234.55	41.10	0.0	56.85		

22	0. 1.	8.81	14.01	1.58	167.54	28.62	0.0	45.31		
22	1. 6.	9.10	17.51	1.65	160.84	33.73	0.0	51.08		
22	6. 11.	9.01	21.40	1.89	167.54	33.14	0.0	60.14		
22	11. 16.	10.96	28.01	2.13	187.64	37.42	0.0	69.21		
22	16. 21.	13.67	22.57	2.40	211.10	40.07	0.0	56.02		
22	21. 26.	11.05	18.68	2.13	201.05	38.36	0.0	34.60		
22	26. 31.	12.31	19.45	2.19	207.75	39.04	0.0	35.43		
22	31. 36.	12.69	19.74	2.30	216.17	39.89	7.05	50.87		
22	36. 41.	11.69	19.74	2.23	219.45	41.54	7.07	51.69		
22	41. 46.	11.93	17.37	2.16	209.62	38.92	5.68	49.23		
22	46. 51.	10.72	16.98	1.99	203.07	38.08	4.97	44.31		
22	51. 56.	11.63	15.79	1.95	186.69	39.13	4.92	42.67		
22	56. 61.	10.50	15.79	1.92	186.69	37.16	0.0	42.67		
22	61. 66.	9.90	15.00	1.99	203.07	39.30	2.54	44.31		
22	66. 73.	11.35	16.58	1.92	206.35	38.71	5.66	42.67		

23	1. 6.	8.42	17.37	1.92	180.14	33.99	3.88	49.23		
23	6. 11.	8.75	15.00	1.81	170.32	29.33	0.0	43.49		
23	11. 16.	6.80	15.79	1.85	163.77	29.90	0.0	44.31		
23	16. 21.	11.48	22.51	2.61	229.27	40.82	0.0	54.97		
23	21. 26.	11.14	18.56	2.09	212.90	39.97	0.0	54.97		
23	26. 31.	11.41	20.53	2.19	222.72	42.59	0.0	59.08		
23	31. 36.	11.44	15.79	2.02	209.62	38.08	0.0	51.69		
23	36. 41.	11.69	16.58	1.92	203.07	39.55	0.0	51.69		
23	41. 46.	11.02	14.61	1.85	203.07	37.99	0.0	50.87		
23	46. 51.	10.78	13.82	1.81	203.07	36.82	0.0	46.77		
23	51. 56.	10.47	14.21	1.85	193.24	35.90	0.0	45.95		
23	56. 61.	11.20	14.61	1.88	203.07	36.82	0.0	46.77		
23	61. 66.	10.93	15.00	1.92	206.35	36.32	0.0	46.77		
23	66. 71.	11.75	19.74	2.27	216.17	38.12	6.71	50.87		
23	71. 76.	9.50	15.96	1.79	202.76	36.86	0.0	46.92		
23	76. 83.	9.23	15.16	1.83	189.68	38.56	0.0	46.11		



NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
25	1. 6.	7.35	11.57	1.52	209.30	33.15	0.0	40.45		
25	6. 11.	7.17	11.57	1.45	202.76	33.11	8.32	40.45		
25	11. 16.	7.32	11.57	1.56	196.22	34.55	6.02	40.45		
25	16. 21.	8.69	11.17	1.66	212.57	37.56	5.39	43.68		
25	21. 26.	10.36	17.16	1.96	274.71	42.96	0.0	50.15		
25	26. 31.	13.32	30.72	2.64	372.82	50.14	7.59	66.33		
25	31. 36.	17.34	43.09	3.25	480.74	61.20	8.83	79.27		
25	36. 41.	18.02	48.68	3.42	510.17	64.13	10.33	88.98		
25	41. 46.	15.08	31.92	2.77	408.79	52.38	5.27	74.42		
25	46. 51.	13.98	30.32	2.64	418.60	49.20	5.20	67.95		
25	51. 56.	14.17	23.94	2.37	327.03	47.32	0.0	59.86		
25	56. 61.	12.89	14.76	1.86	255.08	42.16	0.0	46.92		
25	61. 66.	11.15	13.57	1.69	251.81	36.15	0.0	42.06		
25	66. 71.	14.93	19.15	1.83	402.25	46.72	0.0	51.77		

29	1. 6.	9.82	16.76	1.76	196.22	38.31	0.0	46.11	95.	1.8
29	6. 11.	10.06	16.76	1.76	202.76	36.98	0.0	48.53	95.	1.2
29	11. 16.	11.09	13.97	1.69	192.95	38.10	0.0	46.11	95.	0.4
29	16. 21.	9.85	14.76	1.69	186.41	37.07	0.0	45.30	93.	0.7
29	21. 26.	10.54	19.95	1.89	215.84	42.87	0.0	51.77	66.	1.9
29	26. 31.	15.73	26.43	2.85	292.04	52.32	7.46	67.16	63.	1.8
29	31. 36.	12.48	18.82	2.06	220.81	43.43	4.36	50.16	80.	1.6
29	36. 41.	10.37	15.93	1.80	174.51	39.68	3.63	44.21	84.	1.2
29	41. 46.	10.15	13.39	1.66	170.95	36.41	0.0	42.51	95.	0.7
29	46. 51.	11.01	14.12	1.73	170.95	38.65	0.0	41.66	96.	1.2
29	51. 56.	11.21	13.03	1.73	167.39	39.08	0.0	39.96	93.	0.9
29	56. 61.	10.30	13.76	1.77	170.95	37.53	0.0	42.51	88.	0.8
29	61. 66.	11.26	13.03	1.59	142.46	35.00	0.0	36.56	93.	0.9
29	66. 71.	10.65	14.12	1.73	167.39	39.78	0.0	38.26	100.	1.1
29	71. 76.	9.49	14.12	1.70	163.83	36.05	0.0	36.56	95.	0.9

30	1. 6.	11.97	43.44	2.13	188.76	46.38	28.79	88.42		
30	6. 11.	12.27	33.30	2.16	185.20	44.27	18.46	71.41		
30	11. 16.	10.40	18.82	2.02	224.37	37.99	10.63	53.56		
30	16. 21.	9.47	18.10	2.16	231.50	40.55	4.59	52.71		
30	21. 26.	9.47	13.03	1.88	206.57	39.22	0.0	41.66		
30	26. 31.	8.61	12.31	1.80	195.88	39.38	0.0	39.96		
30	31. 36.	8.69	11.58	1.70	185.20	33.50	0.0	38.26		
30	36. 41.	6.82	10.86	1.66	185.20	33.63	0.0	35.71		
30	41. 46.	9.57	19.91	2.24	249.30	42.09	0.0	51.01		
30	46. 51.	13.04	14.12	2.16	284.92	41.32	0.0	48.46		
30	51. 56.	12.65	13.76	1.91	345.47	38.85	4.38	45.91		
30	56. 61.	11.95	12.42	1.81	279.82	36.84	6.58	48.03		
30	61. 67.	13.06	13.15	2.02	215.25	40.72	6.92	46.38		

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
31	0. 1.	12.09	34.70	2.64	430.49	50.94	8.12	67.91	41.	2.8
31	1. 6.	11.84	33.61	2.53	322.87	49.07	4.72	67.91	40.	3.1
31	6. 11.	12.07	33.61	2.31	283.41	50.23	0.0	61.28	65.	2.0
31	11. 16.	11.35	33.61	2.53	315.70	48.64	4.47	66.25	46.	2.5
31	16. 21.	12.11	31.42	2.53	312.11	51.90	7.03	63.77	48.	1.1
31	21. 26.	11.57	30.68	2.60	287.00	50.02	0.0	62.11	50.	1.8
31	26. 31.	11.77	31.42	2.60	261.88	48.64	0.0	61.28	54.	1.5
31	31. 36.	12.36	33.97	2.64	269.06	52.18	7.14	66.25	39.	2.9
31	36. 41.	11.84	33.61	2.35	258.30	54.15	7.01	63.77	40.	2.4
31	41. 46.	13.20	32.88	2.49	265.47	54.51	5.19	64.60	44.	1.9
31	46. 51.	11.91	34.34	2.53	304.93	55.88	0.0	64.60	36.	2.7
31	51. 56.	13.22	35.07	2.53	315.70	52.18	6.20	65.42	44.	2.2
31	56. 61.	12.07	35.80	2.71	319.28	53.68	6.18	67.91	33.	1.6
31	61. 66.	13.79	37.26	2.75	337.22	53.83	3.98	69.57	24.	1.2
31	66. 72.	10.94	31.05	2.53	301.34	50.62	5.53	62.11	44.	1.8

33	0. 1.	11.66	34.70	2.89	287.00	46.54	11.27	74.53	27.	4.7
33	1. 6.	11.66	29.22	2.71	276.23	43.23	7.72	71.22	40.	2.4
33	6. 11.	12.11	32.15	2.60	261.88	46.05	9.24	70.39	35.	2.5
33	11. 16.	12.07	33.61	2.64	251.12	47.62	8.51	72.88	38.	2.0
33	16. 21.	13.32	30.14	2.44	228.05	46.26	8.00	65.74	48.	2.2
33	21. 26.	12.80	27.94	1.94	231.67	48.37	5.22	59.17	59.	1.3
33	26. 31.	11.28	26.47	2.23	224.43	46.12	7.82	59.99	63.	0.2
33	31. 36.	11.18	25.73	2.34	224.43	43.29	4.32	59.99	63.	0.8
33	36. 41.	11.38	22.79	2.05	202.71	39.25	5.24	53.42	74.	0.6
33	41. 46.	9.57	22.06	2.05	206.34	37.17	4.14	54.24	71.	1.1
33	46. 51.	11.87	24.63	2.23	202.71	39.12	4.14	59.17	59.	1.4
33	51. 56.	10.69	23.53	2.09	206.34	37.47	6.49	55.06	65.	1.6
33	56. 61.	12.14	27.57	2.44	238.91	41.68	6.19	64.92	54.	2.0

34	0. 1.	14.95	36.02	2.98	343.89	45.68	6.55	70.67	18.	2.5
34	1. 6.	13.61	36.39	2.66	224.43	44.57	8.10	71.49	17.	1.9
34	6. 11.	15.30	36.02	2.59	217.20	48.37	7.27	70.67	24.	1.5
34	11. 16.	13.94	32.35	2.48	224.43	45.24	7.13	65.74	25.	1.2
34	16. 21.	14.98	35.66	2.63	246.15	48.44	7.88	72.32	19.	2.8
34	21. 26.	14.31	30.88	2.59	231.67	44.67	7.50	65.74	27.	2.3
34	26. 31.	14.38	34.19	2.80	275.11	49.23	5.24	68.21	32.	3.0
34	31. 36.	15.88	36.76	2.73	296.83	52.57	6.69	69.85	20.	3.2
34	36. 41.	15.18	36.76	2.66	307.69	49.43	6.91	69.85	24.	3.4
34	41. 46.	14.06	30.88	2.59	282.35	40.68	5.93	63.28	33.	4.5
34	46. 51.	14.53	34.19	2.66	289.59	40.78	4.38	69.03	24.	0.7
34	51. 56.	14.43	35.29	2.70	271.49	40.45	6.29	69.85	23.	1.9
34	56. 61.	12.77	30.74	2.91	260.47	41.37	4.66	61.63	32.	2.1
34	61. 66.	12.10	30.37	2.49	271.63	44.97	5.76	64.92	39.	2.1
34	66. 70.	13.02	32.22	2.56	286.51	43.76	8.03	69.03	34.	2.6

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
35	0. 1.	11.65	30.37	2.56	346.05	40.38	17.24	75.60		
35	1. 6.	10.76	22.96	2.27	267.91	37.46	10.82	59.99		
35	6. 11.	12.60	31.85	2.59	275.35	45.47	11.29	62.46		
35	11. 16.	11.75	29.63	2.49	271.63	44.54	10.55	67.39		
35	16. 21.	11.93	25.56	2.31	267.91	45.91	10.72	61.63		
35	21. 26.	13.09	23.70	2.31	241.86	41.13	5.27	59.99		
35	26. 31.	12.15	15.93	1.99	212.09	40.52	4.31	46.02		
35	31. 36.	10.71	17.78	1.95	215.81	35.37	2.20	41.09		
35	36. 41.	10.93	17.04	1.95	193.49	36.21	0.0	45.20		
35	41. 46.	11.23	19.26	2.13	230.70	39.04	0.0	49.31		
35	46. 51.	11.80	25.93	2.49	271.63	44.40	0.0	56.70		
35	51. 56.	9.56	19.26	2.24	241.86	37.57	0.0	49.31		
35	56. 61.	8.40	17.04	1.95	223.26	36.14	0.0	42.73		
35	61. 66.	9.14	18.52	2.13	238.14	41.55	0.0	46.02		
35	66. 71.	9.58	16.67	1.99	253.02	37.18	0.0	46.02		
35	71. 76.	9.92	17.04	2.02	230.70	36.59	0.0	42.73		
35	76. 83.	9.68	17.78	1.99	223.26	34.75	0.0	42.73		

36	0. 1.	9.14	27.04	2.56	334.88	40.21	13.46	69.03		
36	1. 6.	13.81	28.76	2.65	253.61	45.78	7.27	68.95		
36	6. 11.	16.30	29.12	2.86	272.26	51.30	6.49	76.43		
36	11. 16.	17.90	29.49	2.75	268.53	53.26	6.12	70.61		
36	16. 21.	13.93	27.28	2.50	257.34	46.59	2.13	55.66		
36	21. 26.	13.20	20.65	2.29	234.96	42.84	0.0	51.51		
36	26. 31.	12.56	18.43	2.22	223.78	42.94	0.0	49.01		
36	31. 36.	11.73	20.28	2.36	234.96	44.71	0.0	49.84		
36	36. 41.	13.35	19.54	2.11	212.59	42.35	0.0	49.01		
36	41. 46.	10.90	18.43	1.90	193.94	41.19	0.0	43.20		
36	46. 51.	12.54	22.86	2.47	249.88	42.44	0.0	54.00		
36	51. 56.	8.56	19.54	2.22	231.24	41.91	0.0	48.18		
36	56. 61.	7.89	16.96	1.86	201.40	36.21	0.0	39.88		
36	61. 66.	10.13	15.48	1.90	212.59	36.70	0.0	41.54		
36	66. 71.	8.16	17.33	1.79	208.86	35.76	0.0	41.54		

37	0. 1.	14.24	36.50	2.86	440.09	47.16	8.74	70.61		
37	1. 6.	12.03	33.92	2.65	328.21	46.28	4.55	65.63		
37	6. 11.	13.43	36.13	2.61	350.58	45.71	0.0	66.46		
37	11. 16.	13.88	32.44	2.61	324.48	44.17	2.81	64.80		
37	16. 21.	12.72	30.60	2.57	309.56	44.51	4.93	63.14		
37	21. 26.	12.89	23.96	2.29	279.72	39.80	0.0	54.00		
37	26. 31.	15.33	31.71	2.61	331.94	47.60	0.0	64.80		
37	31. 36.	14.19	32.33	2.78	322.66	51.06	6.39	65.51		
37	36. 41.	14.62	24.53	3.14	345.95	58.21	3.31	63.05		
37	41. 46.	14.02	24.53	2.54	309.35	48.35	4.09	55.68		
37	46. 51.	9.78	22.30	2.11	272.76	41.48	2.27	46.67		
37	51. 56.	11.25	27.50	2.64	312.68	42.66	3.31	59.77		
37	56. 61.	11.20	25.27	2.26	306.03	45.59	3.57	51.59		
37	61. 66.	10.40	20.44	2.04	296.05	40.75	2.13	42.58		
37	66. 73.	11.55	27.50	2.57	345.95	45.79	3.55	58.96		

NO	DEPTH	CO	CU	FE	MN	NI	PB	ZN	%SAND	%LI
38	0. 1.	14.43	39.40	3.17	409.15	51.17	6.75	72.06		
38	1. 6.	12.54	26.02	2.54	306.03	43.32	6.33	60.59		
38	6. 11.	12.92	26.76	2.61	332.64	44.40	3.87	55.68		
38	11. 16.	12.38	28.25	2.61	345.95	45.17	3.60	57.32		
38	16. 21.	8.17	17.84	2.11	279.42	43.86	0.0	45.85		
38	21. 26.	7.48	17.10	2.33	259.46	41.48	0.0	45.04		
38	26. 31.	9.55	16.35	2.40	272.76	44.98	0.0	45.04		
38	31. 36.	10.08	16.35	2.78	282.74	46.72	0.0	47.49		
38	36. 41.	9.41	15.98	2.01	246.15	39.42	0.0	39.30		
38	41. 46.	7.61	16.73	1.97	252.81	36.77	0.0	40.12		
38	46. 51.	7.98	17.84	2.08	252.81	39.61	0.0	40.94		
38	51. 56.	8.46	17.84	1.90	239.50	36.05	0.0	38.49		
38	56. 61.	8.80	18.58	2.11	252.81	37.49	0.0	44.22		
38	61. 66.	11.24	19.83	1.77	230.41	40.80	0.0	41.97		

60	0. 1.	14.61	32.04	2.44	385.17	42.72	15.62	77.23	51.	2.5
60	1. 6.	12.39	16.40	1.73	216.66	36.59	12.05	52.89	95.	1.6
60	6. 11.	12.97	18.69	1.94	223.54	37.50	9.22	54.57	88.	1.5
60	11. 16.	12.97	20.21	2.12	237.29	38.45	5.49	54.57	80.	0.7
60	16. 21.	13.14	14.49	1.84	213.22	36.23	5.63	50.37	93.	0.9
60	21. 26.	12.33	13.35	1.77	196.02	34.63	5.34	47.01	95.	1.7
60	26. 31.	13.89	13.73	1.84	202.90	34.81	6.42	45.33	95.	1.6
60	31. 36.	13.08	13.73	1.87	202.90	36.59	5.06	43.65	94.	2.0
60	36. 41.	12.99	13.73	1.84	192.59	35.32	4.39	41.97	95.	1.8
60	41. 46.	11.67	13.73	1.77	189.15	34.38	5.74	41.57	93.	1.8
60	46. 51.	12.39	13.35	1.77	192.59	35.87	3.03	41.97	94.	1.6
60	51. 56.	12.47	12.20	1.84	199.46	35.87	6.39	41.57	94.	1.2
60	56. 61.	13.40	12.20	1.91	192.59	34.31	6.07	41.13	96.	1.0
60	61. 66.	12.47	12.59	1.84	199.46	31.90	7.81	41.57	92.	1.1
60	66. 71.	11.55	12.20	1.91	192.59	33.73	6.13	41.13	95.	0.9
60	71. 78.	11.24	12.20	1.91	192.59	33.73	3.02	41.13	94.	1.1

TRACE METAL VALUES IN PPM, FE IN %

PB VALUES BELOW DETECTION LIMITS WHERE LISTED AS 0.0