

C.1

MANGANESE CHEMISTRY
IN THE FRASER ESTUARY

by

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ABSTRACT

The Fraser Estuary was investigated five times under varying flow regimes. The surface distribution of dissolved manganese consistently exhibited a maximum value at a salinity ranging from 4 to 12 ppt. Experimental results and field data suggest this peak does not result from the desorption nor dissolution of riverborne suspended particulate manganese. The excess metal is derived from the estuarine bottom sediments.

Desorption or dissolution of manganese from the estuarine bottom sediments resuspended due to the advancing salt wedge enhances the dissolved manganese concentration in the bottom waters, especially in the toe of the salt wedge. This manganese enrichment may also be influenced to a lesser extent by the concurrent release of some interstitial water with enriched dissolved manganese concentrations due to the in situ reduction of amorphous manganese oxides. The subsequent entrainment and mixing of water from the toe of the salt wedge into the outflowing river water causes a downstream increase in the dissolved manganese content, and eventually determines the peak manganese concentration and salinity. Further downstream mixing with saline waters having relatively low manganese levels causes surface concentrations to decrease. Thus, the dissolved manganese distribution can be explained in terms of two conservative dilution curves which intersect at the manganese peak.

The dissolved oxygen generally behaves conservatively in both the surface and bottom waters of the Fraser Estuary. The removal of alkalinity may occur at low salinity, however,

alkalinity exhibits conservative behaviour through most of the salinity range. The surface distribution of pH can be replicated theoretically only when mixing in the surface is considered as a two step process.

The alkalinity behaves conservatively in the surface waters of the Strait of Georgia. The pH and dissolved oxygen display seasonal variations related to primary productivity and mixing processes.

The distribution of dissolved manganese in surface waters of the Strait of Georgia is determined mainly by the dilution of Fraser River water. Bottom waters have enhanced dissolved manganese concentrations due to reductive remobilization of manganese from the sediments. Concentrations of dissolved manganese at mid-depths are determined by seasonal variations in the stability of the water column. Depth profiles of suspended particulate manganese indicate increasing concentrations with depth. This may result from the oxidative precipitation of manganese and/or the resuspension of bottom sediments.

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1. INTRODUCTION

1.1 The Estuarine Environment

Cameron and Pritchard (1963) define an estuary as "a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water deriving from land drainage". This refers only to a positive type estuary (Pritchard, 1952) where river runoff and precipitation exceed evaporation. From a chemical point of view, the estuary is a mixing zone of fresh and sea water which produces compositional gradients (Burton, 1976).

Chemical gradients arise when river water, having low pH and ionic strength and high concentrations of several trace metals, nutrients and suspended sediment, mixes with sea water having high pH and ionic strength but low concentrations of these trace metals, nutrients and suspended sediment. The extent of mixing can be monitored with salinity measurements. Several studies cited by Liss (1976) indicate that the concentrations of most of the major constituents in an estuary are determined solely by physical mixing processes. Furthermore, although the composition of the river salt matrix differs from that of sea salt, the low salt concentration in river water ensures that the salinity through most of the mixing zone is determined by sea water electrolytes. Thus, salinity can be considered to be a "conservative index of mixing".

In estuarine chemistry, the concepts of conservative and non-conservative behaviour are important in examining chemical

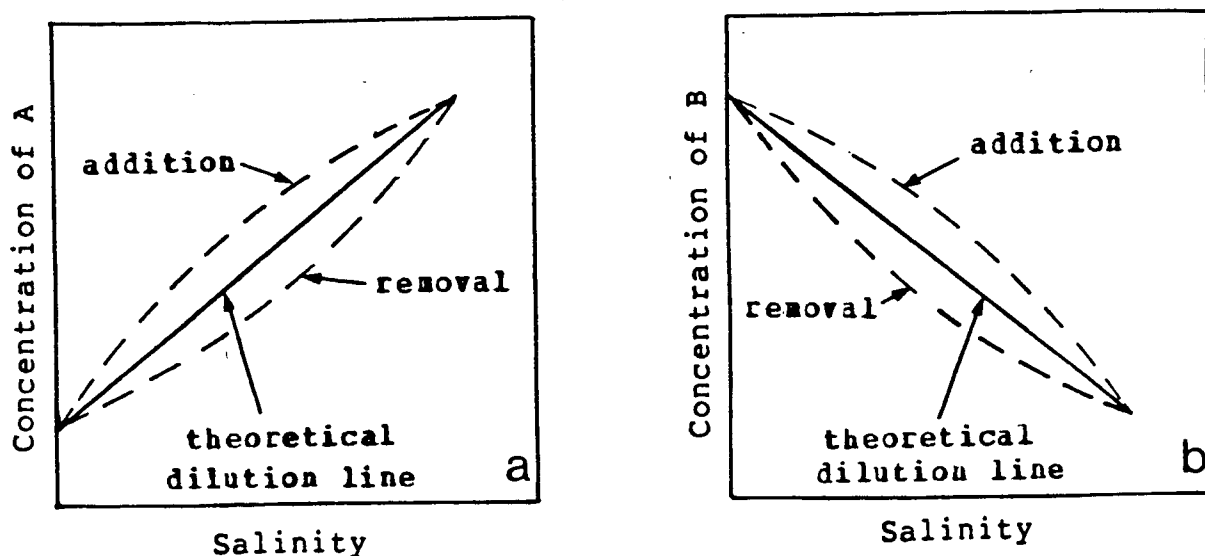


Figure 1 Conservative and non-conservative behaviour during estuarine mixing of single river and sea water end members (Liss, 1976).

gradients. A component is said to behave conservatively if the concentration of that component in the estuary depends solely upon the extent of mixing between single river and sea water end members. Graphically, the concentration of a given component would vary linearly with salinity and may exhibit a positive (A) or negative (B) slope depending upon the relative concentrations in river and sea water (see Figure 1).

Departure from this theoretical mixing line indicates non-conservative behaviour, that is, the concentration of the component is affected by chemical and/or biological processes. Values below the ideal mixing curve indicate removal of the component while levels above the theoretical dilution line indicate an estuarine input.

Chemical constituents in natural waters are often categorized as "dissolved" or "particulate". Proposed by

Goldberg et al. (1952), "dissolved" material is operationally defined as that material which passes through a filter with a nominal pore size of 500 nm while "particulate" material is retained on the filter. By this method, the dissolved component may include polymers and colloids as well as the material which is in true solution.

Physico-chemical processes within the estuarine environment affect the dissolved and particulate constituents independently but can also stimulate interaction between these components (Burton, 1976). The chemical speciation of dissolved constituents may change due to variations in the concentrations and type of ligands present while particulate components may be deposited due to hydrodynamic factors and flocculation processes. Interactions between the two phases can cause transfer of material from the dissolved to the particulate component by flocculation, precipitation, adsorption onto particulates or absorption by organisms. Alternatively, dissolved material may be released from the particulate matter by dissolution, desorption or biological processes.

1.2 Manganese Case Studies

Manganese and iron are biochemically active transition metals. Geochemically they are subject to drastic changes in solubility depending upon the pH and Eh conditions of natural waters. Furthermore, the oxides and hydroxides of these elements are efficient scavengers of other metals (Krauskopf, 1956; Hem, 1978) and may influence the concentrations of toxic metals in the estuarine environment. Factors controlling the

distribution of iron in estuaries are well understood (Boyle et al., 1977; Sholkovitz, 1978). Iron is removed from solution either by precipitation as humates and/or by the flocculation of colloidal iron hydroxide species. While in some instances the removal of iron may be accompanied by manganese precipitation, the chemistry of manganese is not necessarily coupled to that of iron.

Several field studies of manganese have been conducted indicating wide variations in estuarine behaviour. Conservative behaviour of dissolved manganese has been observed in the St. Lawrence Estuary (Subramnian and d'Anglejan, 1976) and the Beaulieu Estuary (Holliday and Liss, 1976; Moore et al., 1979). However, in the case of Holliday and Liss (1976), their assessment is questionable as they chose to ignore elevated concentrations at low salinities.

Most field studies indicate that dissolved manganese behaves non-conservatively and two processes have been identified, one or both of which may be occurring concurrently in a given estuary. Firstly, an increase in the manganese concentration over a conservative dilution curve has been observed at low salinities indicating that there is a local source of dissolved metal, (Holliday and Liss, 1976; Evans et al., 1977; Morris et al., 1978; Duinker et al., 1979b; Wollast et al., 1979). Secondly, a deficiency of dissolved manganese relative to conservative mixing has been found at higher salinities indicating removal (Graham et al., 1976; Duinker et al., 1979b).

The peak manganese concentration has been attributed to

desorption from the particulate material by Graham et al., (1976) in Narragansett Bay. Evans and Cutshall (1973) found that 30 to 60% of the riverborne suspended ^{54}Mn was released upon contact with sea water in the Columbia Estuary. However, mixing experiments by Sholkovitz (1979) and Duinker et al. (1979b) could not detect the release of manganese from riverine suspended material from the Tay and Rhine Rivers, respectively. Furthermore, in considering the mass balance in the Newport Estuary, Evans et al. (1977) found that the particulate material alone could not account for the excess manganese. They proposed that the estuarine sediments acted as a manganese source. Subsequently, Sanders (1978a) and Eaton (1979) have shown that sediments in the Calico Creek and Chesapeake Bay, respectively, may supply overlying estuarine water with dissolved manganese. Direct measurements by Graham et al., (1976) indicated a manganese flux from the sediments of $2 \pm 1 \mu\text{g cm}^{-2} \text{ day}^{-1}$, while crude estimates by Duinker et al. (1979b) were on the order of $1 \mu\text{g cm}^{-2} \text{ day}^{-1}$.

Precipitation of manganese, possibly as hydrous manganese dioxide, is considered to be the major process causing removal in the lower reaches of some estuaries. This mechanism has been reported for three rivers in Georgia (Windom et al., 1971), Narragansett Bay (Graham et al., 1976), and the Rhine and Scheldt Estuaries (Duinker et al. 1979b). Since the stability constants of manganese humates are very low (Mantoura et al., 1978), Sholkovitz (1978) attributed dissolved manganese removal in his mixing experiments to the catalytic effect which hydrous ferric oxide has on the oxidation and precipitation of Mn^{2+} from

aerated water.

The general model of manganese behaviour proposed by Evans et al. (1977) involved a recycling mechanism similar to the estuarine nutrient trap. Dissolved manganese precipitates as manganese dioxide in the lower reaches of the estuary. This particulate manganese is carried upstream and deposited in the upper reaches of the estuary. There, reductive remobilization of manganese from the sediment into overlying low salinity waters maintains the maximum dissolved concentration. This recycling may be reinforced by a comparable biological cycle. Desorption from riverborne particulate material may also contribute to the manganese peak. Since the Newport Estuary was exporting manganese during the surveys conducted by Evans et al. (1977), they proposed a mass balance was attained in the upper reaches of the estuary by either an episodic deposition of large quantities of particulate material or a continual supply of bedload material.

Extending this hypothesis offshore, Sundby (1977) and Yeats et al. (1979) suggested that manganese in riverborne detritus which escapes the estuarine zone may be remobilized from coastal sediment. Such a process in the Gulf of St. Lawrence causes a dissolved manganese flux an order of magnitude higher than that introduced by rivers.

Many early estuarine field studies involved either dissolved or particulate manganese measurements only, and often were restricted to the surface waters. A field programme in the Fraser River was proposed to investigate manganese chemistry in a salt wedge type estuary, as classified by the scheme of

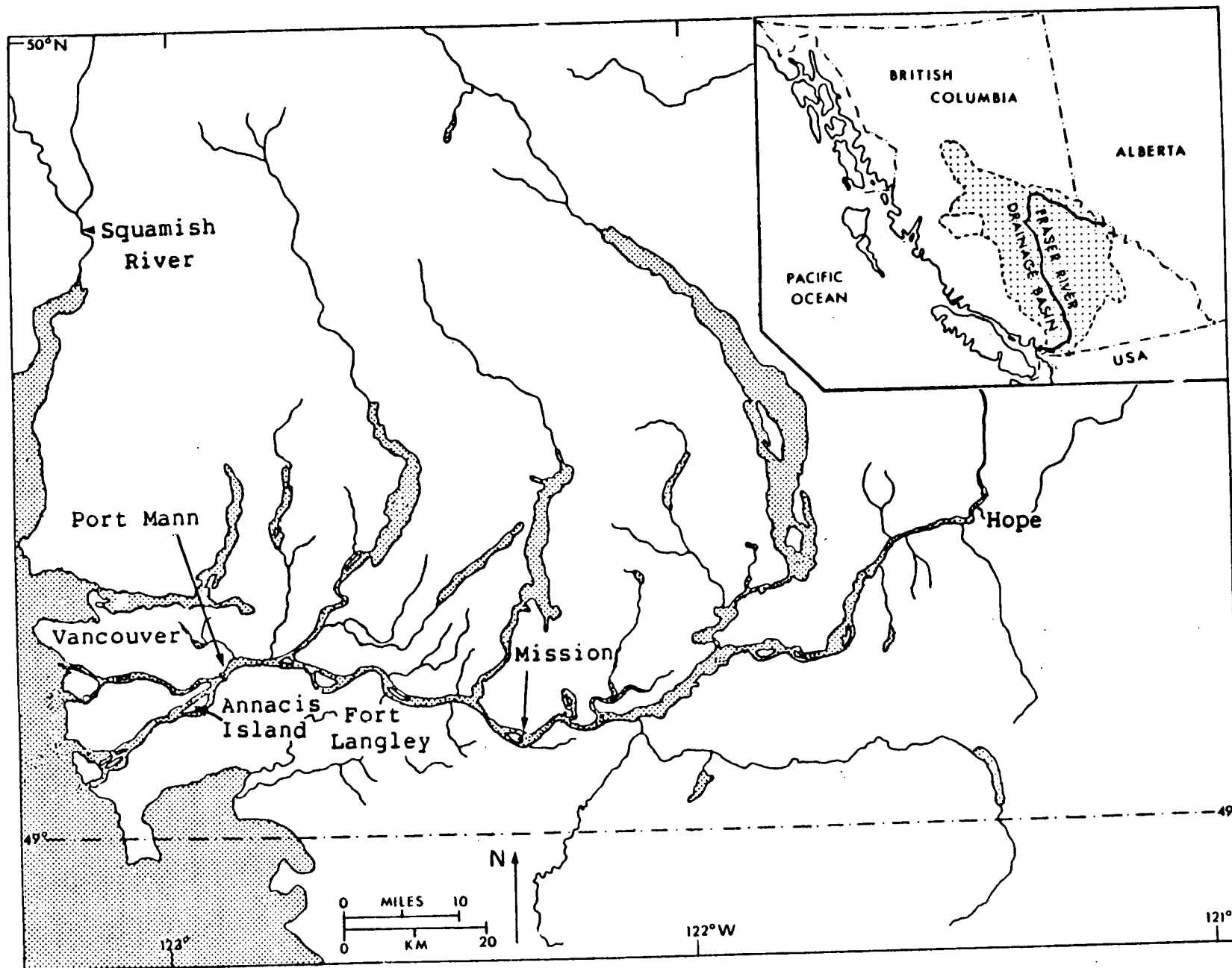


Figure 2 The lower Fraser River valley.

Cameron and Pritchard (1963), and to test the recycling model of Evans et al. (1977). The distribution of dissolved and particulate manganese in both the surface and bottom waters would be established to determine which features of the recycling model were present. Also estuarine sediments would be examined to evaluate their potential in contributing dissolved metal into overlying waters. The Strait of Georgia was included in the study area since it often incorporates the high salinity mixing zone of Fraser River water. Furthermore, sediment within the strait may contribute significant quantities of manganese to the system.

1.3 The Fraser Estuary

The Fraser Estuary, in southwest British Columbia (Figure 2), is supplied by the Fraser River which is approximately 1400 km long and drains an area of 233,000 km² (Hoos and Packman, 1974). The mean daily discharge rate at Hope for 1978 and 1979 was 2370 m³/sec (Water Survey of Canada, 1978 and 1979). The Fraser River is subject to drastic seasonal variations in flow as illustrated in Figure 3 which depicts the daily average discharge rate measured at Hope for 1978 and 1979. Minimum discharge rates (approximately 700 m³/sec) occur in February and March while rapid snow melt in the watershed causes the freshet (7000-8500 m³/sec) early in June in most years.

Tides in the estuary are a mixture of diurnal and semi-diurnal tides. The range varies from 5m during spring tides to 1m or less during neap tides.

Hodgins (1974) classifies the Fraser Estuary as a unique

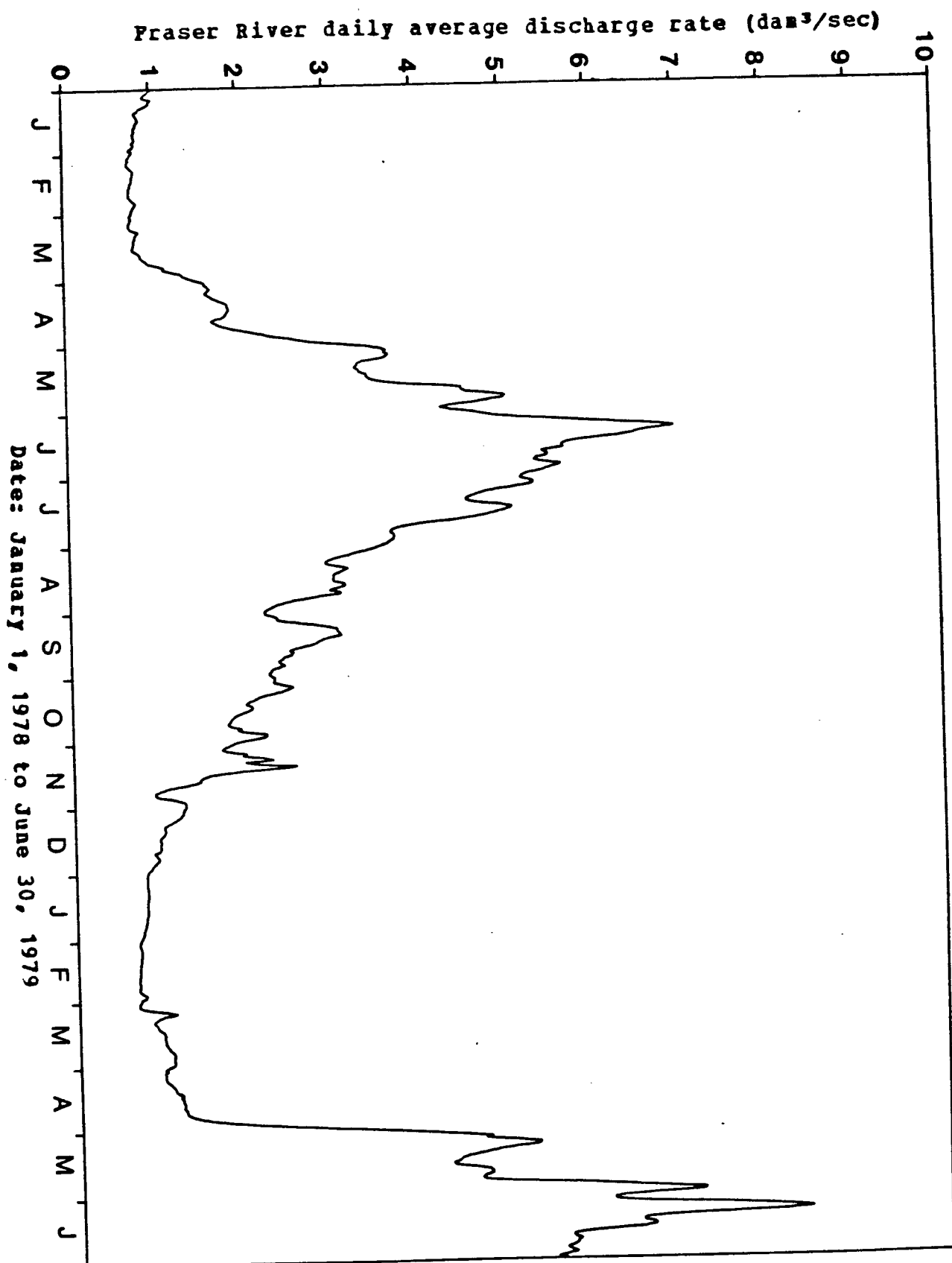


Figure 3 Hydrograph of the Fraser River measured at Hope (Station No. 08MF005) for 1978-1979 (Water Survey of Canada, 1978 and 1979).

example of a moderately stratified estuary (Cameron and Pritchard, 1963), which is flushed of salt each tidal cycle. The penetration of the salt wedge depends upon the rate of river discharge and the state of the tide. During winter months salt water may intrude as far upstream as Annacis Island (Figure 2) but during the freshet the salt wedge does not extend upstream past Steveston.

The river bifurcates at New Westminster and further divides into numerous lesser channels downstream. This study was confined to the main arm, 10 to 15 m deep, which accounts for 80 to 85% of the flow.

1.4 The Strait of Georgia

Trending southeast-northwest, the Strait of Georgia is situated between Vancouver Island and the British Columbia mainland and has connections to the Pacific Ocean at both ends, in the south via Juan de Fuca Strait and in the north via numerous narrow passages (Figure 4). The basin is 220 km long with an average width of 33 km and a mean depth of 156 m (Waldichuk, 1957).

Under the broad definition of Cameron and Pritchard (1963) the Strait of Georgia is considered to be an estuary. Furthermore, it can be classified as a positive fjord-like estuary (Pritchard, 1952). The Fraser River contributes approximately 80% of the total runoff entering the strait and at any time the volume of fresh water in the strait is equivalent to 16 months of Fraser River discharge (Waldichuk, 1957).

Waldichuk (1957) reviewed the physical oceanography of the

Strait of Georgia and attributed the general counter-clockwise circulation to the tides, runoff and wind. The tides cause intensive mixing in the southern portion of the strait, especially in the winter. Winds contribute to mixing the surface waters and affect the circulation of the surface brackish layer.

Brackish surface waters form as the outflowing Fraser River water entrains and mixes with saline water. This water exits the strait mainly through the southern passages, the entrained sea water being replaced at depth by an influx of oceanic water from the Juan de Fuca Strait. However, strong tidal action in these passages causes this compensating flow to be a mixture of these two water masses rather than "pure" sea water. The specific characteristics of this water mass vary seasonally.

Bottom Water is formed in the late autumn as dense water from the Juan de Fuca Strait intrudes into the mixing zone of the southern passages. In the summer months a warm, highly saline Intermediate Water mass is formed in these channels. During cold winters, Intermediate Water may also be formed in the northern parts of the Strait of Georgia.

2. METHODS

2.1 Sea Water Samples

2.1.1 Sampling Programme

The sampling programme extended from January 1978 until May 1979 and required fourteen cruises. Throughout this seventeen month period parameters monitored were temperature, salinity, oxygen, pH, alkalinity, dissolved and particulate manganese, particulate aluminium and iron, and in some instances the total suspended particulate concentration.

Station locations are illustrated in Figures 4 and 5; the positions are recorded in Appendices A.1 and A.2. Appendix A.3 provides a complete summary of cruise dates, ships used and field areas visited.

For purposes of discussion the area investigated can be divided into three regions:

- (1) Fraser River Estuary, functionally defined by geographic considerations as extending from New Westminster to Sand Heads
- (2) Strait of Georgia
- (3) Station 15, near Sand Heads

The Fraser River Estuary was investigated five times during the sampling programme. Attempts were made to sample under varying flow regimes. Table I gives an indication of the daily average discharge of the Fraser River at Hope on the days that the estuary was investigated (Water Survey of Canada, 1978 and 1979).

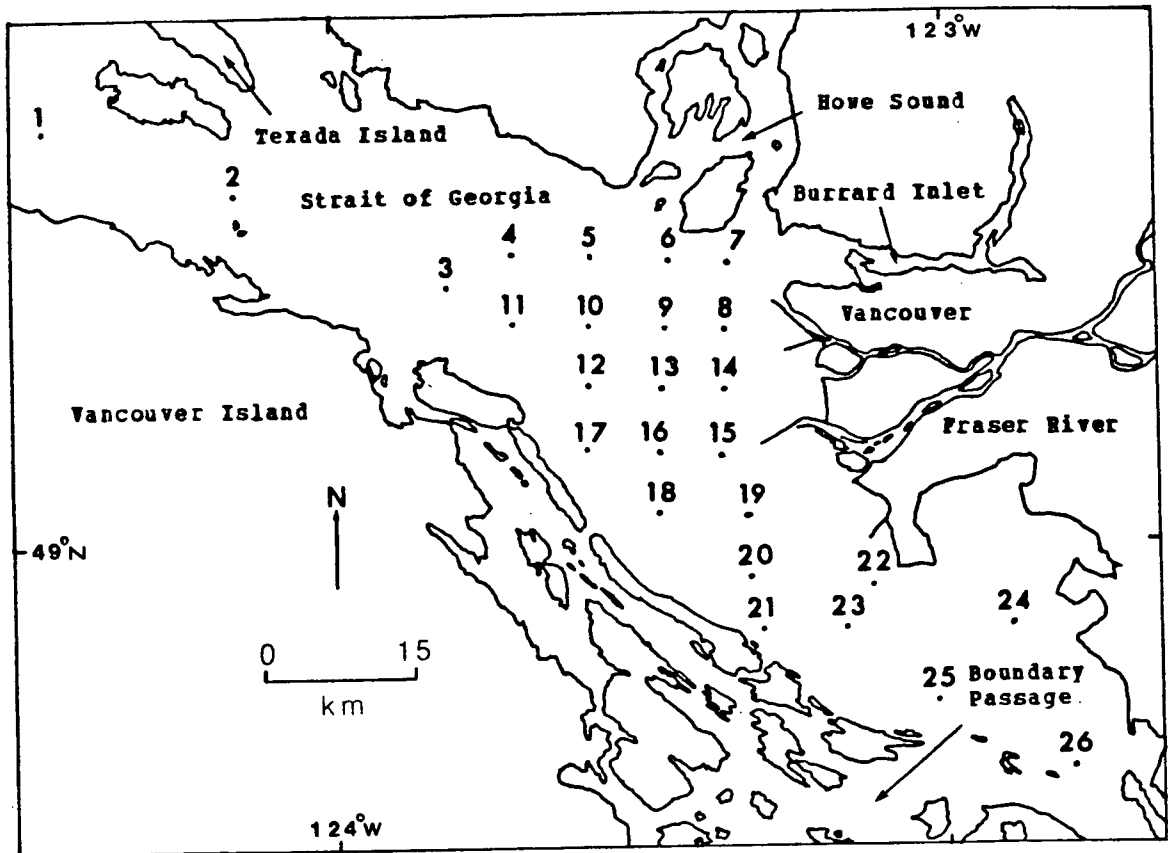


Figure 4 Station Locations in the Strait of Georgia.

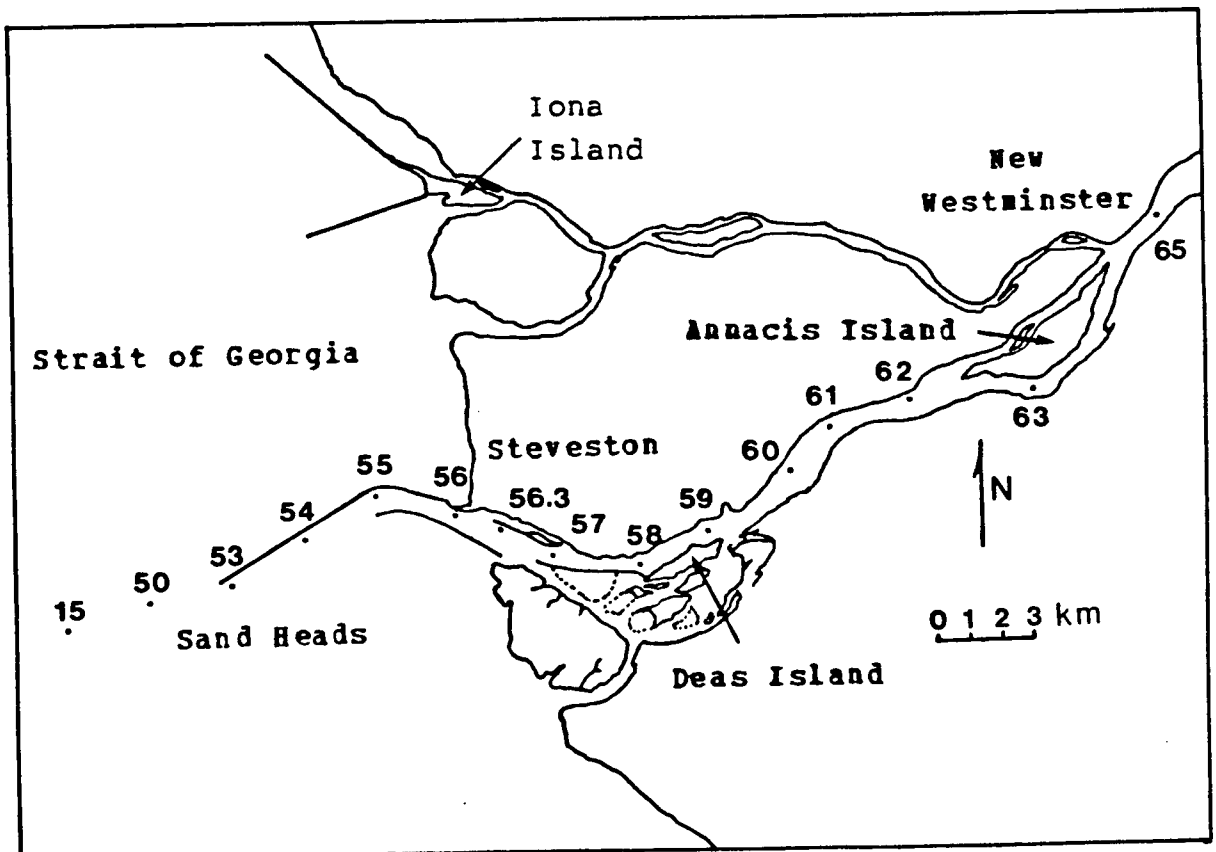


Figure 5 Station Locations in the Fraser Estuary.

TABLE I Daily Average Discharge Rate of the Fraser River during Estuarine Cruises

Cruise Number	Dates	Daily Average Discharge Rate at Hope (m ³ /sec)
78-04	Mar 22, 1978	951
78-11	Jul 19, 1978	4730
78-16	Oct 17, 1978	1950
	18	1880
	19	1840
79-01	Jan 4, 1979	816
79-12	May 30, 1979	7160
	31	7120

The dates and values of the seasonal maxima and minima daily discharge rates are presented in Table II. Estuarine cruises were conducted twice during periods of low river run-off, twice at different intermediate discharge levels, and once as the river was approaching the peak in the freshet.

Water was collected from 1m below the surface and 1m above the bottom so as to obtain a range of salinities from 0 to 30 ppt in both surface and bottom waters. Salt wedge samples were collected during cruises in 1978; however, ice conditions in January and the high flow rates in May made it impossible to get extensive data in 1979.

Four systematic surveys of the Strait of Georgia were conducted. In all, 26 stations from Texada Island to Boundary Passage were occupied (Figure 5); however, complete depth

TABLE II Seasonal Extremes in the Daily Average Discharge Rate of the Fraser River

Dates	Daily Average Discharge Rate at Hope (m ³ /sec)
Feb 5, 1978	736
Jun 8, 1978	6970
Mar 3, 1979	694
Jun 9, 1979	8390

profiles were obtained at only four locations: Stations 1, 3, 15 and 25. The remaining stations were sampled at 1m and 5m depths in 1978 but only at 1m during 1979 cruises. Station 15 was investigated on nine other occasions.

With few exceptions water samples were collected in one litre polypropylene NIO bottles. Since the entire contents of one bottle were necessary to ensure complete recovery of the particulate matter (Duinker et al., 1979a), a second bottle was required for the measurement of other water parameters. Therefore, a pair of NIO bottles was mounted on an aluminium frame equipped with a bottom self-tripping mechanism which could also be activated for surface samples by means of a nylon rope. Dual casts were performed at those stations where a depth profile was obtained. In instances where the total suspended particulates were measured, the samples were collected using a separate 250 ml bottle which was mounted piggy-back on the NIO bottle and tripped simultaneously.

River water samples from Fort Langley (Station 70) were collected with a plastic bucket on a nylon rope. This method was also necessary at some stations on Cruise 79-01 due to the presence of ice on the river. Bucket samples can be differentiated from NIO samples since their depths are recorded in the data file (Appendix B) as 0m as opposed to 1m.

2.1.2 Temperature, Salinity, and Oxygen

Temperature, salinity, and oxygen were measured by standard procedures employed at the UBC Department of Oceanography. Specific details of the techniques and data are presented in departmental Data Reports 45 (1979) and 47 (1980). Briefly, oxygen concentrations were determined by Winkler titration (Carritt and Carpenter, 1966) and salinities were measured with a Guildline Autosol Model 8400 Salinometer. The lower limit for the reliability of the conductivity:salinity relationship corresponds to a conductivity ratio of 0.100 or salinity of 2.85 ppt. Temperatures recorded to ± 0.01 °C were measured with reversing thermometers. Supplementary estuarine temperatures were measured with a Beckman RS5-3 Portable Salinometer/thermometer.

2.1.3 Alkalinity and pH

Samples for pH and alkalinity were drawn after those for salinity into Nalgene polypropylene 50 ml wide-mouth and 250 ml bottles respectively.

The pH samples and standard buffer solutions were placed

immediately into a water bath with no temperature control. After ambient temperature equilibrium was attained, the pH was measured with a Beckman Model GS pH Meter. Electrodes were standardized at a pH near 7.5 with a 0.03043 M disodium hydrogen phosphate and 0.008695 M potassium dihydrogen phosphate buffer solution prepared according to Mattock (1963). As recommended by Gieskes (1969), the in situ pH was calculated by applying a correction factor of 0.0114 pH units per degree difference between in situ temperature and the temperature of pH measurement. Including errors associated with temperature corrections, the precision (one standard deviation) of in situ pH measurements is estimated to be ± 0.03 pH units.

Alkalinity samples were stored in a refrigerator at approximately 4°C until subsequent analysis in the laboratory by the method of Anderson and Robinson (1946). That is, 25 ml of 0.0100N HCl was added to a 100ml aliquot of sample. The resultant pH was measured on a Beckman Model GS pH Meter. Electrodes were standardized at a pH near 4 with a 0.05M potassium hydrogen phthalate buffer solution also prepared as described by Mattock (1963). The alkalinity, in meq/l, was calculated from the expression:

$$\text{alkalinity} = 2.500 - 1250 (a_{H^+}/f_{H^+})$$

where a_{H^+} = activity of hydrogen ion

f_{H^+} = hydrogen ion activity coefficient

Values for f_{H^+} at varying salinities were estimated graphically by plotting data from Anderson and Robinson (1946). At low salinities, f_{H^+} was assumed to approach 1.0 as the salinity approached 0.0 ppt.

Six replicate analyses of a sea water sample (salinity of 30.7 ppt) with a mean alkalinity of 2.11 meq/l yielded a standard deviation of ± 0.01 meq/l. Similarly, six replicate analyses of a river water sample (salinity of 0.0ppt) with a mean alkalinity of 1.26 meq/l yielded a standard deviation of ± 0.01 meq/l.

2.1.4 Total Suspended Particulates

Total suspended particulate concentrations were determined by the method of Cranston and Buckley (1972). The complete contents of the piggy-back sampler were emptied via a funnel into a washed and dried 400 ml glass bottle. As soon as possible after collection the volume was measured in a 500 ml graduated cylinder and then suction filtered through preweighed Nuclepore polycarbonate filters having a nominal pore size of 400 nm. The glass bottle and cylinder were rinsed into the filtration unit with small aliquots of distilled deionized water. The filter was further rinsed with small aliquots of water to remove sea salt, placed in a washed petri dish and frozen for storage. Blanks were prepared by filtering 300 ml of distilled deionized water.

Subsequently the filters were oven dried at 60 °C for two hours, then left overnight to attain equilibrium with ambient temperature and humidity. Weights were recorded at least twice to ± 0.01 mg on a Mettler H20 Balance. Weights prior to filtration were obtained in a similar manner after soaking the filter for an hour in distilled deionized water.

Blanks were negligible. The precision (one standard

deviation) of the sediment weight was ± 0.05 mg in samples ranging from 0.50 to 600.00 mg. The water volume was 250 ml ± 5 ml. This indicates a precision between 5 and 2% for sediment concentrations varying from 4 to 2400 mg/l. Only four samples had suspended loads less than 4 mg/l.

2.1.5 Dissolved Manganese

To minimize sources of contamination, equipment necessary for the processing and storage of trace metal samples was acid-cleaned prior to use. This process involved rinsing first with hot 6N HCl then several times with distilled deionized water. Gelman Metrical GA-6 Membrane Filters, with a nominal pore size of 450 nm, were decontaminated by soaking at least thirty minutes in 5% potassium dihydrogen phosphate and then in distilled deionized water.

To avoid possible problems associated with differential settling of particulate material in the sampler, the complete contents of an NIO bottle were emptied into an acid-cleaned 64oz PVC jug. As soon as possible after collection the volume of the sea water was measured in a 2 l polypropylene graduated cylinder and then the sample was suction filtered through previously decontaminated filters. After discarding the first 100 to 300 ml of sample, the filtrate was stored in acid-cleaned 500 ml Nalgene polypropylene bottles which had been rinsed with a small amount of the filtered sea water. Aqueous samples were acidified to a pH of approximately 1.5 with 2 ml of concentrated HCl and stored at room temperature until analysed. Although storage for some months prior to analysis was unavoidable,

depletion of soluble manganese by precipitation or adsorption onto container walls was not anticipated to be a problem. Experiments by Subramanian et al. (1978) indicated that after thirty days no manganese loss occurred from river and sea water samples acidified to a pH of 1.6.

The filters were stored in acid-cleaned plastic petri dishes at room temperature until analysed.

Blanks were prepared at sea by filtering 600 ml of distilled deionized water, the filters and filtrate processed as mentioned for sea water samples.

Dissolved manganese was determined by flame atomic absorption spectrophotometry (AAS) following a three stage extraction technique similar to that described by Thomas and Grill (1977) and Grill (1978). In brief, the manganese was chelated with sodium diethyldithiocarbamate (NaDDC), extracted with iso-amyl acetate (IAA), and back extracted into acid chlorine water; finally, for analysis by AAS the manganese was again extracted with NaDDC into methyl iso-butyl ketone (MIBK). Specific details of the procedure follow. First it should be noted that although dissolved manganese concentrations were determined on a volume basis, that is $\mu\text{g/l}$, they are recorded as ppb (parts per billion or 10^{-9}) ignoring the small conversion factor.

All organic solvents required, that is carbon tetrachloride, IAA and MIBK, were redistilled from reagent grade solvents. In the case of IAA, a single 2 l bottle was recycled for all analyses. A 10% (W/V) NaDDC solution was prepared fresh daily by dissolution of reagent grade NaDDC in distilled

deionized water and decontaminated by successive extractions with carbon tetrachloride until the organic phase remained colourless. A 1M Tris buffer was prepared by the dissolution of reagent grade tris-hydroxymethylaminomethane in distilled deionized water and adjusting the pH to approximately 7.5 with concentrated HCl. Following the addition of 5 ml of NaDDC solution, the Tris buffer was decontaminated with carbon tetrachloride as above. Acid chlorine water was made in 100 ml batches by the addition of 1 ml concentrated HCl to distilled deionized water saturated with chlorine gas.

A 450 ml aliquot of sample was transferred to an Erlenmeyer flask. After addition of 5 ml each of the NaDDC solution and Tris buffer, the pH was adjusted to the range 6.80 to 7.05 with concentrated ammonia solution and dilute HCl. The manganese was extracted into 20 ml of IAA by vigorous mixing for 15 minutes with a magnetic stirrer. Following 5 minutes for phase separation, the upper organic phase was transferred via pipette into a 125 ml separatory funnel. The extraction was repeated twice with 10 ml aliquots of IAA. The combined organic extracts were back-extracted by shaking for one minute first with 5 ml of acid chlorine water and then twice with 4 ml aliquots of distilled deionized water. These aqueous extracts were combined, giving a solution pH near 1.5, and stored in an acid-cleaned 30 ml Nalgene polypropylene bottle for subsequent analysis.

Later, the sample concentrate was emptied into a glass beaker. After the addition of 1 ml of Tris buffer and adjusting the pH to 7 as before, the sample was transferred to a 25 ml

mixing cylinder. A 0.5 ml aliquot of NaDDC solution was added together with sufficient distilled deionized water to give a final volume of 20 ml. Following the addition of 5 ml of MIBK, vigorous shaking for 1 minute, and 15 minutes for phase separation, the organic phase was aspirated directly into an air-acetylene flame and the absorbance measured at 279.6 nm on a Techtron AA-4 Atomic Absorption Spectrophotometer. Water saturated MIBK was aspirated to establish a baseline and the measured absorbances were corrected for the reagent blank. Concentrations were determined from calibration curves prepared by subjecting aqueous manganese standards to the same treatment as the sample concentrates. Blanks rarely exceeded the detection limit of 0.1 ppb.

Nine replicate determinations of a sea water sample with a mean concentration of 2.66 ppb gave a standard deviation of 0.12 ppb (4.5%). Five incremental standard additions of 2.2 ppb manganese were recovered from Strait of Georgia sea water with an efficiency of 102%. These values agree with those of Grill (1978) who reported a precision of 4.0% at the 2 ppb level and an extraction efficiency of 97.8%.

While this method is laborious and time consuming it has two main attributes. First, the extractable manganese is consistently recovered with an efficiency closely approximating 100%, whereas the recovery rate of a single extraction technique such as that of Brooks et al. (1967) may exhibit a salinity dependence, thereby introducing a potential source of error in estuarine analyses. Secondly, after concentrating the metal by a factor of 90, the manganese concentration is well above

detection limits; moreover, the metal is in an MIBK medium that virtually eliminates any possible matrix effects.

2.1.6 Particulate Metal Analyses

Particulate manganese, iron and aluminium concentrations were determined by flame atomic absorption spectrophotometry following an acid digestion procedure modified from Riley (1958). Five ml of a 4:1 nitric:perchloric acid mixture were added to filters placed in teflon digestion bombs. The nitric acid was evaporated under an infra-red lamp until perchloric acid fumes were generated. After the addition of 4 ml of concentrated hydrofluoric acid, the reaction vessels were placed overnight in a vented oven at 80°C. The next day the hydrofluoric acid was evaporated under infra-red lamps. The remaining perchloric acid was diluted to 10 ml and stored in acid-cleaned, dried 30 ml Nalgene polypropylene bottles until analysed.

Manganese and iron were determined by aspirating the resulting digests into an air-acetylene flame and measuring the absorbances at 279.6 nm for manganese and 248.5 nm or 372.3 nm for iron. Aluminium was determined with a nitrous oxide-acetylene flame at 396.3 nm. In all cases the measured absorbances were corrected for reagent and filter blanks. For the manganese analyses, background absorbances were corrected with a deuterium background corrector (Varian BC-6). The concentrations were evaluated from calibration curves of metal standards in 10% perchloric acid.

To test for possible volatile losses during the digestion,

TABLE III Analysis of Certified Reference Materials

Element	Canadian Rock Sample (% dry weight)	
	MRG-1	SY-2
Mn MnO R. V. (1)	0.136±0.003 0.175 0.17	0.256±0.009 0.330 0.32
Al Al ₂ O ₃ R. V. (1)	3.98±0.51 7.52 8.50	6.86±0.40 13.0 12.12
Fe Fe ₂ O ₃ R. V. (1)		4.40±0.30 6.29 6.28

(1) Recommended Value (Abbey, 1980)

1 ml of a standard solution with 5 ppm Mn and 250 ppm Al was treated in the prescribed manner. For 15 replicate analyses, mean recovery rates and standard deviations were $99.5 \pm 3.8\%$ and $97.0 \pm 7.1\%$ for Mn and Al respectively. Reagent blanks were 0.3 μg and 1.1 μg respectively.

To determine both the precision and accuracy of the technique, certified reference materials were analyzed. About 50 mg samples of Canadian Rock Standards SY-2 and MRG-1 were digested. The results, presented in Table III, indicate relative standard deviations of 2.2% (MRG-1) and 3.5% (SY-2) for manganese, 6.8% (MRG-1) for iron, and 13% (MRG-1) and 5.8%

(SY-2) for aluminium. The concentrations of manganese and iron give good agreement with the values recommended by Abbey (1980). The non-systematic discrepancies in the aluminium determinations may result from matrix effects.

Concerning units, concentrations of manganese, iron and aluminium were measured on a volume basis but have been referred to as $\mu\text{g/kg}$ instead of $\mu\text{g/l}$, again ignoring the conversion factor. Thus, throughout the text particulate metal concentrations in ppb or ppm refer not to metal concentrations in particulate material on a dry weight basis but rather actual concentrations of particulate metal in sea water.

2.2 Sediment Samples

2.2.1 Collection and Storage

All information regarding collection dates, sampling devices and sample sites of sediments is summarized in Appendix A.4.

Shipek grab samples were obtained from selected stations in the Fraser Estuary. Representative samples from the centre of the bucket were placed in whirl-pak polyethylene bags and stored in a refrigerator near 4°C .

Gravity cores were taken at Station 15 on Cruises 78-01 and 79-02. These were stored at ambient (winter) temperatures for shipment to the laboratory.

Repeated attempts at gravity coring in the Fraser River and Estuary failed due to the coarse sandy nature of the sediment. However, cores were collected by divers in February 1979 and

January 1980. A plastic core-liner was pushed into the sediment, capped top and bottom in situ and transported to the surface. These cores were frozen as soon as possible to prevent loss of interstitial water by drainage from the sandy sediment. Samples of bottom water for salinity determination were collected at the same time as cores in January 1980 by opening standard glass storage bottles at depth.

At the laboratory, and as soon as possible after collection, the cores were divided into 3 cm long sections. After thawing where necessary, core segments and some grab samples were squeezed as described in the following section. Finally, the sediments were stored in polyethylene whirl-pak bags and frozen until subsequently analysed.

2.2.2 Interstitial Water Analyses

Interstitial water was extracted from the samples using a plastic sediment squeezer of the type described by Reeburgh (1967). The samples were squeezed under nitrogen gas through Gelman Acropor AN-450 filters (nominal pore size 450 nm, pretreated as described for filters in Section 2.1.5) directly into 30 ml Nalgene polypropylene bottles which had previously been acid-cleaned and dried.

Care was taken to minimize the length of time the sediments were exposed to the atmosphere. Although oxidative loss of soluble Mn^{2+} from interstitial water has been suggested by Lyons and Gaudette (1978), the work of Sanders (1978b) indicates that the periods of air exposure are too brief to cause appreciable decreases in Mn^{2+} concentrations.

Upon squeezing, a few drops of the interstitial water were removed via a Pasteur pipette and placed in an Endeco Type 102 Refractometer to estimate the salinity. Although measurement of known salinity samples indicated an accuracy of only ± 0.5 ppt, this was sufficient for comparative purposes.

The pH of the remaining interstitial water sample was adjusted to approximately 1.5 with a few drops of concentrated HCl and stored for subsequent analysis of dissolved manganese. Manganese concentrations were determined by AAS by aspirating the acidified interstitial water directly into an air-acetylene flame and measuring the absorbance at 279.6 nm. Background absorbances were corrected with a deuterium background corrector (Varian BC-6) and the concentrations evaluated from calibration curves derived from measurements on manganese standards prepared in acidified sea water.

2.2.3 Ammonium Oxalate Extraction of Sediments

To extract amorphous manganese and iron oxides from the sediment, samples were treated in the dark with the 0.2M ammonium oxalate / 0.2M oxalic acid (pH 3.0) reagent following Schwertmann (1964). After sediments were oven dried at 110°C for three hours, they were ground with an agate pestle and mortar to pass through a No. 140 nylon mesh (105 μ m opening). About 100 mg of sediment was placed in an acid-cleaned 100 ml brown polypropylene Nalgene bottle. A 50 ml aliquot of the oxalate solution was added, the suspension shaken vigorously for two hours and then suction filtered through Nuclepore filters

(with a nominal pore size of 400 nm) into an acid-cleaned teflon beaker. The bottle and filtration unit were rinsed a few times with distilled deionized water to ensure all resistant sediment was quantitatively transferred to the filter. The leachate was made up to a volume of 100 ml in an acid-cleaned 100 ml Nalgene polypropylene volumetric flask and then stored in an acid-cleaned 100 ml Nalgene polypropylene bottle. The filter was stored in an acid-cleaned plastic petri dish.

The oxalate-leachable manganese was analysed by flame AAS following the NaDDC/MIBK extraction procedure, previously described in Section 2.1.5 for sea water concentrates, using a 15 ml aliquot of the oxalate digest solution. The concentration was evaluated from calibration curves prepared by similar extraction of manganese standards from 0.1M ammonium oxalate/0.1M oxalic acid. Reagent blanks were determined by subjecting a 50 ml aliquot of the working oxalate solution to the complete procedure described.

The precision of the technique was estimated from five replicate analyses of a sediment sample from the Fraser Estuary. The results, presented in Table IV, indicate that the mean oxalate-leachable manganese content on a dry weight basis was 111 ppm with a standard deviation of 5 ppm (4.4%). The reagent blank had a manganese concentration of 2 ppm based on a 100 mg sample.

TABLE IV Replicate Manganese and Aluminium Analyses of an Estuarine Sediment

Sample 80-56.2	Metal Concentration (on a dry weight basis)			
3-6 cm	Ammonium Oxalate Leachable Mn (ppm)	Ammonium Oxalate Resistant Mn (ppm)	Total Mn (ppm)	Ammonium Oxalate Resistant Al (%)
1	112	375	487	4.58
2	105	397	502	4.81
3	118	478	596	5.34
4	108	466	574	5.27
5	111	454	564	5.40
Mean	111	434	545	5.08
Std Dev	4.8	45.3	47.5	0.36
RSD	4.4%	10.4%	8.7%	7.2%

2.2.4 Total Metal Content of Sediments

The oxalate-resistant fraction of the sediment retained by the filter was analysed for manganese and aluminium after digestion with nitric/perchloric/hydrofluoric acid as described for particulate samples in Section 2.1.6. On some occasion a black residue, presumed to be resistant organic material, remained after the digestion procedure and, where the amount of this refractory organic material seemed excessive, the digests were filtered through Nuclepore filters (with a nominal pore size of 400 nm) prior to analysis by AAS. Dilution up to a

TABLE V Comparison of Total Mn and Al Content in Surficial
Estuarine Sediments Collected during Cruise 79-12

Station	Mn (ppm) ⁽¹⁾		Al (%) ⁽¹⁾	
	A	B	A	C
3	1840	---	10.4	7.30
15	330	346	7.22	4.74
53	514	524	8.72	5.44
54	498	551	6.99	5.48
55	542	591	5.55	5.03
56	425	468	5.41	5.29
59	447	480	6.07	5.48
65	477	509	5.86	5.21

Column A Total $\text{HNO}_3/\text{HClO}_4/\text{HF}$ digestion only

Column B Mn concentration: Sum of oxalate
extractable and resistant metal

Column C Al concentration: Oxalate-resistant metal
only

(1) Concentrations measured on a dry weight basis

factor of 10 was necessary in some cases to ensure final metal concentrations were within the linear range defined by the working standards.

For comparative purposes 100 mg samples of dried, ground sediment from Cruise 79-12 were also digested in the nitric/perchloric/hydrofluoric acid mixture without prior oxalate extraction. A comparison of total manganese content by the two procedures is given in Table V together with aluminium concentrations. Column A gives metal concentrations, on a dry weight basis, determined by an acid digest without prior oxalate extraction. Manganese concentrations, recorded in column B, are the sum of oxalate-leachable and oxalate-resistant components

and agree within the precision of the technique (one standard deviation) with values in column A. Aluminium concentrations in column C are determined from only the oxalate-resistant components of the sediments; any aluminium extracted by the oxalate was not analysed and this may account for the lower values. While aluminium may be extracted from some amorphous oxides (such as gibbsite), some aluminosilicates may be susceptible to dissolution. Consequently, oxalate-extractable manganese concentrations may also include contributions from these sedimentary components.

The precision of the single-step digestion technique was evaluated with certified Canadian reference materials as indicated in the analysis of particulate samples in Section 2.1.6, while the precision of the acid digestion following oxalate extraction was determined by analysing five replicates of an estuarine sediment (Table IV). Mean concentrations and standard deviations of residual manganese and aluminium were 434 ppm \pm 45.3 ppm and 5.08% \pm 0.36%, respectively. This indicates a relative standard deviation of 10.4% for Mn and 7.2% for Al. However, it can be shown that the relative standard deviation for the total manganese, that is the sum of oxalate-leachable and resistant fractions, is only 8.7%.

2.2.5 Grain Size Analysis

Grain size analyses were carried out using the dry sieving method described by Carver (1971). Sediments were washed to remove sea salt, centrifuged and oven-dried at 40°C. This may cause some cementation of the fine-grain fraction of the clay

minerals. After allowing the samples to equilibrate overnight with ambient temperature and humidity, they were weighed and dry sieved by shaking for 15 minutes through a graded series of brass sieves. Each sediment size fraction was subsequently weighed.

3. ALKALINITY AND PH DISTRIBUTION IN THE FRASER ESTUARY

3.1 Introduction

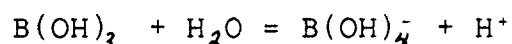
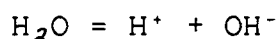
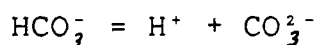
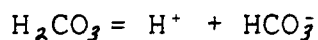
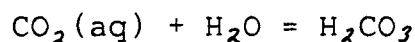
Alkalinity and pH are important parameters in solution chemistry and affect several processes. The pH is a measurement of hydrogen ion concentration while the alkalinity reflects the proton deficiency of the weak acid anions present in the solution (Stumm and Morgan, 1970). The alkalinity is operationally defined as the amount of hydrogen ions required to titrate sea water to the bicarbonate end point. This titration necessarily includes all weak acids with dissociation constants less than the first dissociation constant of carbonic acid. Since the contribution of most weak acids is small, only boric and carbonic acids need to be considered in oxygenated waters. Alkalinity and pH are defined by :

$$\text{pH} = -\log (a_{\text{H}^+})$$

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+]$$

where a_{H^+} = hydrogen ion activity

The pH and alkalinity are interrelated because of their mutual dependence on the carbonate and borate systems, as defined by the reactions:



As a consequence of the above equilibria, processes influencing the concentration of dissolved carbon dioxide perturb the pH of sea water. Thus, carbon dioxide generation via respiration or the oxidative decay of organic matter results in a decrease in pH. Alternatively, carbon dioxide loss by photosynthetic uptake or evasion to the atmosphere causes the pH to rise.

A number of studies of the alkalinity of estuarine waters have been conducted. Alkalinity was found to be conservative in the Columbia (Park et al., 1972) and St. Lawrence Estuaries (Pelletier and Lebel, 1979; Lebel and Pelletier, 1980). However, Wong (1979) observed apparent non-conservative behaviour in the initial mixing zone of the James River in Chesapeake Bay.

Several investigations of the pH of estuarine waters indicate that the hydrogen ion concentration varies with salinity in such a way as to develop a pH minimum at low salinity. This occurs when sea water mixes with river water having a lower pH and has been observed in the Scheldt, Rhine and Tamar Estuaries (Mook and Koene, 1975; Wollast et al., 1979; Morris et al. 1978).

Morris et al. (1978) attributed this behaviour to biological processes. They found the pH minimum associated with a decrease in dissolved oxygen content, an increase in dissolved organic carbon (DOC) concentrations and, a peak in chlorophyll levels. They suggested that halophobic plankton encountering a sudden increase in ionic strength disintegrated, releasing high concentrations of DOC thereby supporting a large population of

oxygen-utilising bacteria. Alternatively, Mook and Koene(1975) proposed that the pH minimum resulted from the rapid increase with salinity of the first and second dissociation constants of carbonic acid. They verified this supposition with laboratory experiments, titrating river water with sea water, and developed a mathematical model that allowed them to calculate pH as a function of salinity. Since their model was used to examine data for the Fraser River, it is worth discussing in some detail.

Several parameters are required to calculate the pH of a water sample. The salinity and temperature determine the apparent dissociation constants of carbonic acid via the expressions of Edmond and Gieskes (1970):

$$pK'_1 = 3404.71/T + 0.032786T - 14.7122 - 0.19178Cl^{1/3}$$

$$pK'_2 = 2902.39/T + 0.02379T - 6.4710 - 0.4693Cl^{1/3}$$

where Cl = chlorinity of the water

T = absolute temperature

Mook and Koene (1975) defined the following expressions applicable at low salinities:

$$pK'_1 = 3404.71/T + 0.032786T - 14.8435 - 0.08921Cl^{1/2}$$

for $0 \leq Cl \leq 9.0$ ppt

$$pK'_2 = 2902.39/T + 0.02379T - 6.4980 - 0.7531Cl^{1/2}$$

for $0 \leq Cl \leq 0.005$ ppt

Using the above relations to evaluate pK'_1 and pK'_2 , the concentrations of carbon dioxide, bicarbonate ion and carbonate ion can be calculated from the carbonate alkalinity (CA) by means of the following expressions (Skirrow, 1975):

$$[CO_2] = a_{H^+}^2 D$$

$$[\text{HCO}_3^-] = a_{\text{H}^+} K'_1 D$$

$$[\text{CO}_3^{2-}] = K'_1 / K'_2 D$$

$$\text{where } D = \text{CA} / (a_{\text{H}^+} K'_1 + 2K'_1 / K'_2)$$

$$\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

The total inorganic carbon content (TC) is defined by:

$$\text{TC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

If $Q = \text{TC}/\text{CA}$, then:

$$Q = (a_{\text{H}^+}^2 + a_{\text{H}^+} K'_1 + K'_1 / K'_2) / (a_{\text{H}^+} K'_1 + 2K'_1 / K'_2)$$

Hence, the pH can be calculated from the quadratic expression:

$$a_{\text{H}^+}^2 + a_{\text{H}^+} K'_1 (1 - Q) + K'_1 / K'_2 (1 - 2Q) = 0$$

In calculating the estuarine pH distribution, Mook and Koene (1975) assumed that the titration alkalinity and total inorganic carbon content were conservative. Titration alkalinities were then corrected for borate contribution giving the carbonate alkalinity. Using b to represent the extent of brackishness, the CA and TC at any chlorinity (salinity) in the estuary are thus given by the expressions:

$$\text{Cl} = (1-b)\text{Cl}_f + b\text{Cl}_m$$

$$\text{CA} = (1-b)\text{CA}_f + b\text{CA}_m$$

$$\text{TC} = (1-b)\text{TC}_f + b\text{TC}_m$$

where subscripts f and m denote the values of fresh and marine end members respectively.

Since $\text{TC}_f = Q_f \text{CA}_f$ and $\text{TC}_m = Q_m \text{CA}_m$; and defining $X = \text{CA}_f / \text{CA}_m$, they could determine Q for any point in the estuary by:

$$Q = \{(1-b)Q_f X + bQ_m\} / \{(1-b)X + b\}$$

To implement the model, Mook and Koene (1975) considered the mixing two water masses at constant temperature. The

properties of the end members explicitly defined were: salinity, alkalinity and pH (which also establishes the total inorganic carbon content). The theoretical pH at any salinity could then be evaluated and the development of the pH minimum at intermediate salinities clearly shown.

Unfortunately, the assumption of conservative behaviour of alkalinity and total inorganic carbon may not be valid for estuarine waters. As previously mentioned, Wong (1979) postulated that alkalinity behaved non-conservatively in the James River Estuary. More important, however, may be biological influences. Prolific productivity in estuaries is well documented (Head, 1976) and may cause carbon dioxide depletion in surface waters. Alternatively, organic matter supplied to bottom waters and sediments may be oxidized. Carbon dioxide generation by organisms and its hydration reactions occur sufficiently rapidly, compared to the residence times of estuarine water, to be of considerable consequence.

The model also assumes that the two end members have the same temperature, and hence, mixing throughout the estuary is isothermal. However, when this is not the case, the apparent dissociation constants of carbonic acid may vary with both temperature and salinity in the lower reaches of an estuary.

The distribution of alkalinity and pH in the Fraser Estuary will be discussed in this chapter. The model of Mook and Koene (1975) will be used to examine the pH data. Dissolved oxygen data, together with a brief discussion, have been included due to the importance of biological processes in modifying the pH of sea water.

3.2 Results

3.2.1 Alkalinity Data

The alkalinity of the estuarine waters was measured on four cruises. The results, plotted versus salinity, are presented in Figures 6a through 6d for Cruises 78-04, 78-11, 78-16, and 79-01, respectively.

Cursory inspection of the data reveals a number of general features. At any time of the year the alkalinity appears to behave conservatively over a wide salinity range. That is to say, the alkalinity persists in being a linear function of salinity even though there are variations in the slope which may reflect temporal influences. Furthermore, sampling depth appears to have little effect on this feature other than to introduce some scatter to the data. This is most evident in October 1978 (Cruise 78-16, Figure 6c).

It should be noted, however, that the alkalinity is not linearly dependent on the salinity over the complete range of salinities sampled. Extrapolation of a linear relationship that best fits the higher salinity data would consistently result in predicting fresh water alkalinity values below those actually observed. Furthermore, deviations from such a relationship are evident below salinities in the range 2 to 8 ppt. While the salinity at which the linear relationship is initiated varies from one cruise to another, in most cases the paucity of data renders it impossible to establish a specific value.

Variations in the river water alkalinity are apparent from one cruise to the next. The alkalinity ranged from a minimum of

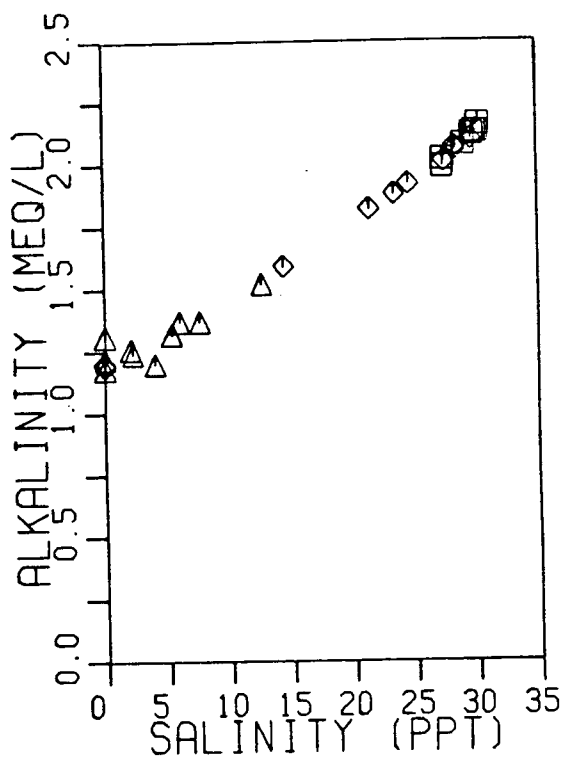


Figure 6a Cruise 78-04

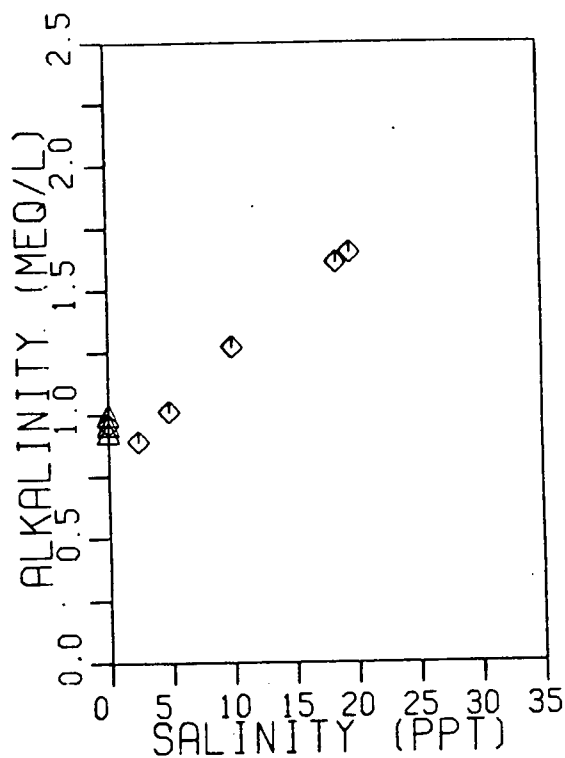


Figure 6b Cruise 78-11

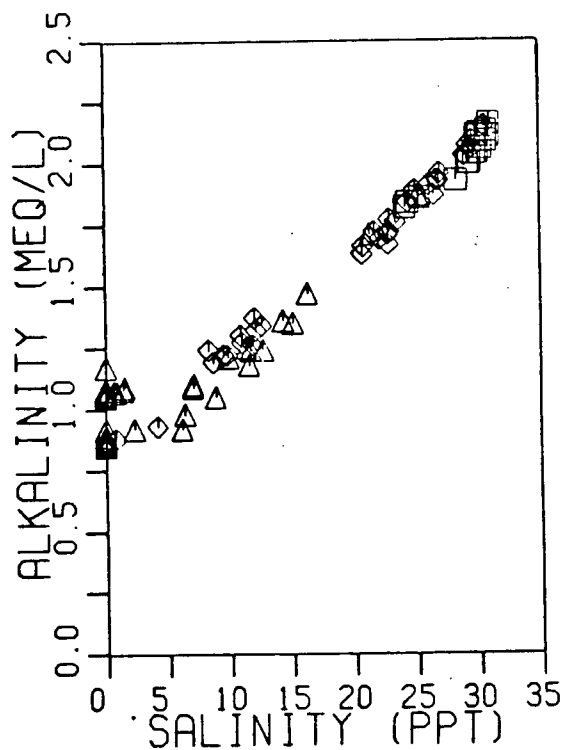


Figure 6c Cruise 78-16

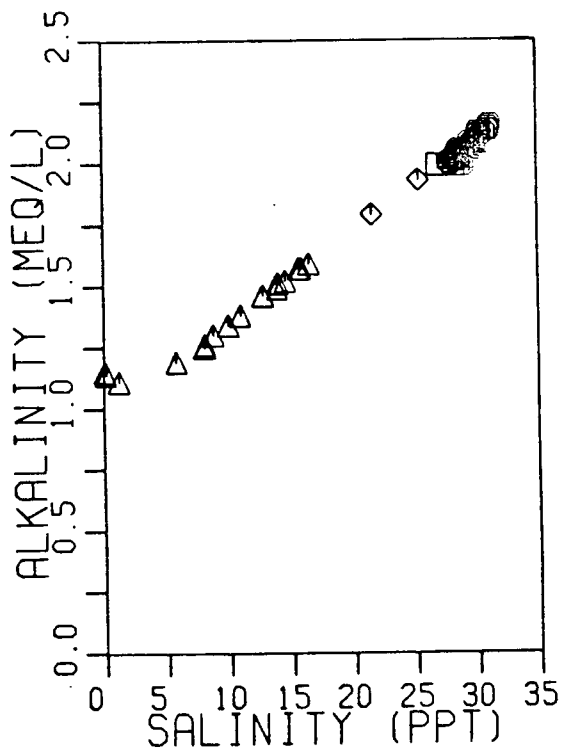


Figure 6d Cruise 79-01

FIGURE 6 Alkalinity data plotted versus salinity for Cruises 78-04, 78-11, 78-16, and 79-01. Symbols: \square data at all depths for Station 15; \circ data at all depths for other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

0.81 meq/l (Cruise 78-04) to a maximum of 1.31 meq/l (Cruise 78-07). However, short term fluctuations of the same magnitude were observed during Cruise 78-16. On the final day of a three day sampling programme in October the alkalinity dropped from values always greater than 1.0 meq/l (maximum value 1.17) to alkalinities less than 1.0 meq/l (minimum value 0.85). This decrease is evident in Figure 6c.

Maximum alkalinities of sea water in the Strait of Georgia tends to fall into the range 2.0 to 2.2 meq/l, depending on the salinity.

3.2.2 Dissolved Oxygen Data

The dissolved oxygen data from the Fraser Estuary, plotted versus salinity, are shown in Figures 7a through 7d for Cruises 78-04, 78-16, 79-01, and 79-12, respectively. Figures 7c and 7d include data from stations throughout the Strait of Georgia.

As best illustrated in Figures 7a and 7c, the dissolved oxygen generally exhibited conservative behaviour in the surface waters of the Fraser Estuary. Non-conservative behaviour was observed in the surface waters of the lower reaches of the estuary during Cruise 78-16 (Figure 7b) and throughout the estuary during Cruise 79-12 (Figure 7d). However, extensive data from salt wedge waters collected during Cruise 78-16 (Figure 7b) indicated that the dissolved oxygen behaved conservatively in bottom waters with salinities less than 27 ppt.

Samples from the Strait of Georgia, including Station 15, exhibit scatter throughout the year. Non-conservative behaviour

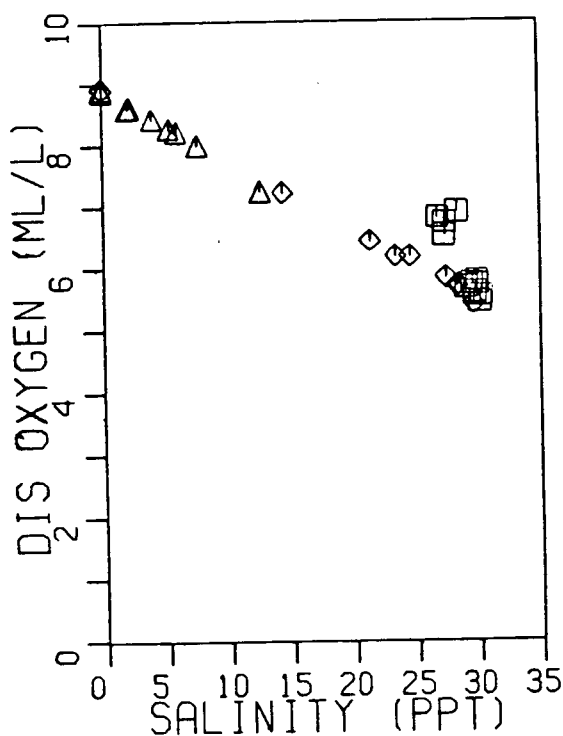


Figure 7a Cruise 78-04

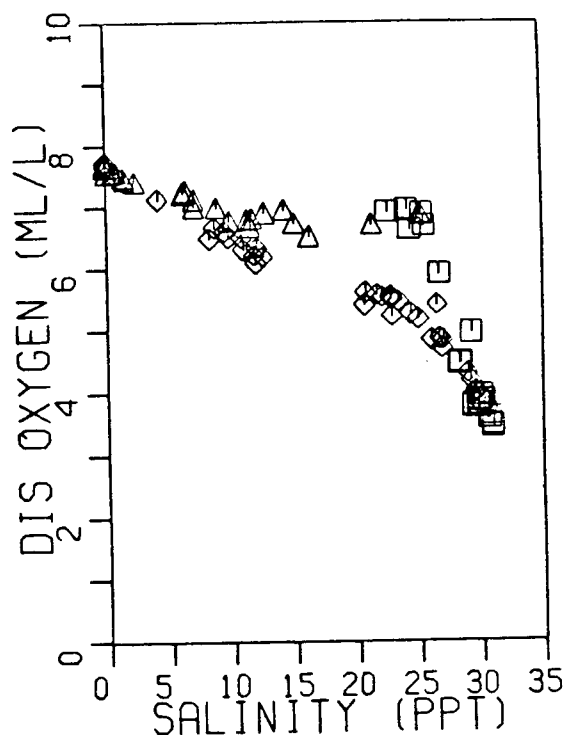


Figure 7b Cruise 78-16

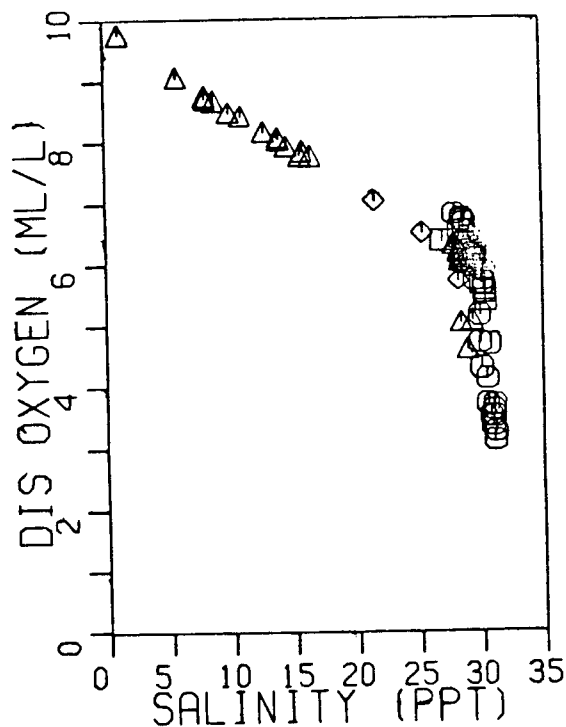


Figure 7c Cruise 79-01

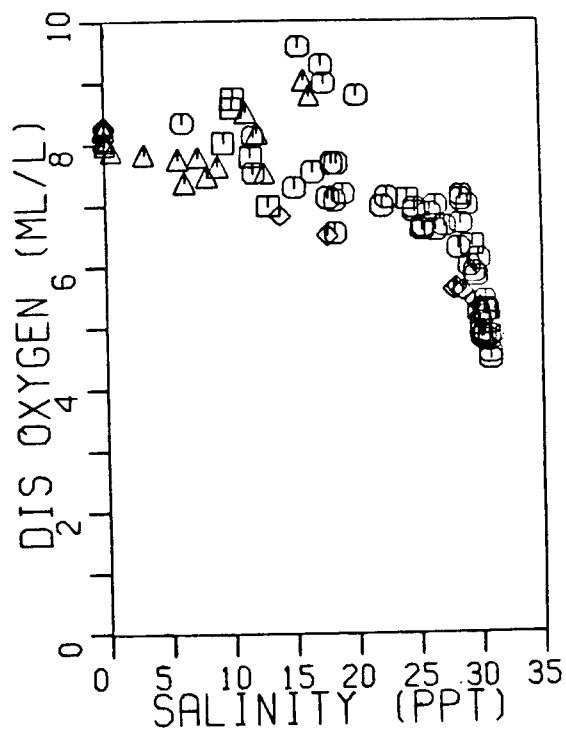


Figure 7d Cruise 79-12

FIGURE 7 Dissolved oxygen data plotted versus salinity for Cruises 78-04, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

occurs because dissolved oxygen concentrations are influenced by biological processes.

3.2.3 pH Data

Estuarine pH measurements from Cruises 78-04, 78-16, 79-01, and 79-12 are plotted versus salinity in Figures 8a through 8d. In March 1978 (Cruise 78-04, Figure 8a) the pH varied little, staying in the range 7.56 to 7.77. The pH values in the Fraser River were very similar to those of surface waters in the Strait of Georgia as characterized by Station 15. However, lower pH values were observed at mid-salinities in the estuary. The scatter evident at higher salinities reflects the wider pH range characteristic of the deeper water column at Station 15.

Considerably more pH data were collected in October 1978 (Cruise 78-16, Figure 8b) and three distinct features can be distinguished. Considering the pH of surface waters only, values were lower in the Fraser River than observed in the Strait of Georgia. The mixing curve for these two end members exhibits a pronounced pH minimum near a salinity of 2 ppt. The pH decreases with depth at Station 15. Bottom samples in the estuary appear to have a uniform pH near 7.8 at salinities less than 23 ppt. At higher salinities the pH decreases to values similar to those in the deep waters of the Strait of Georgia.

In January 1979 (Cruise 79-01, Figure 8c) the same general trend for surface waters can be seen although insufficient data are available to specify the salinity of the pH minimum. Waters throughout the Strait of Georgia, both at the surface and at depth, exhibit pH values lower than those observed in the

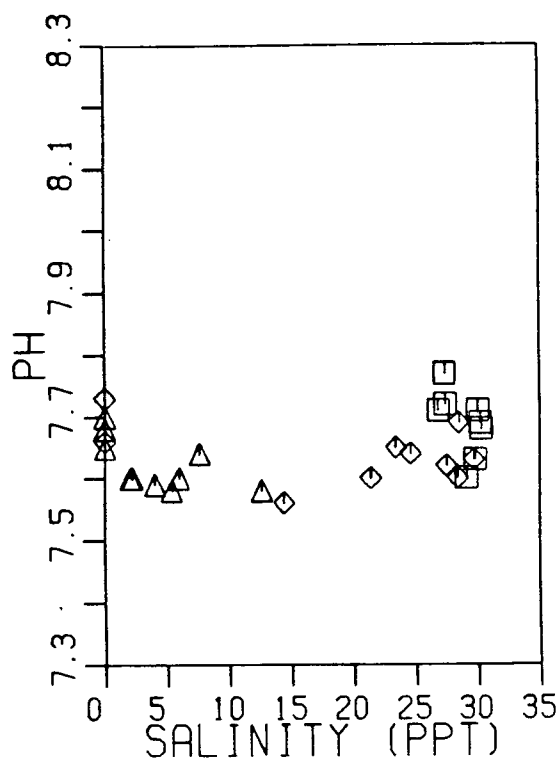


Figure 8a Cruise 78-04

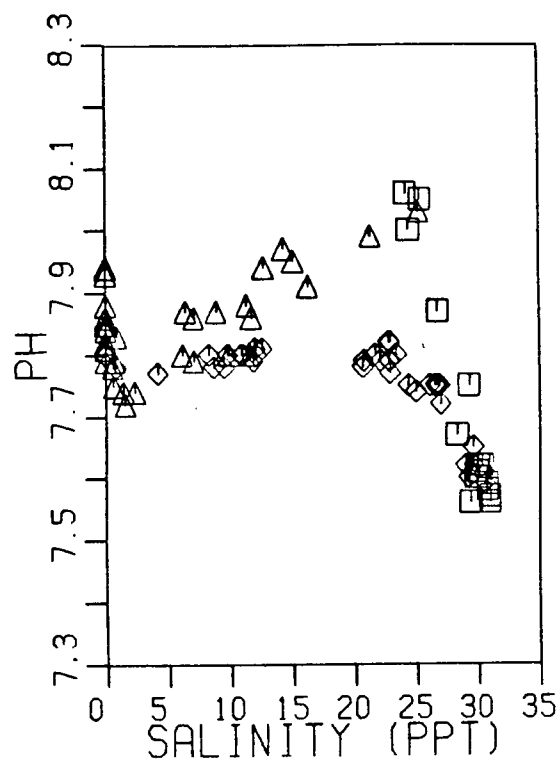


Figure 8b Cruise 78-16

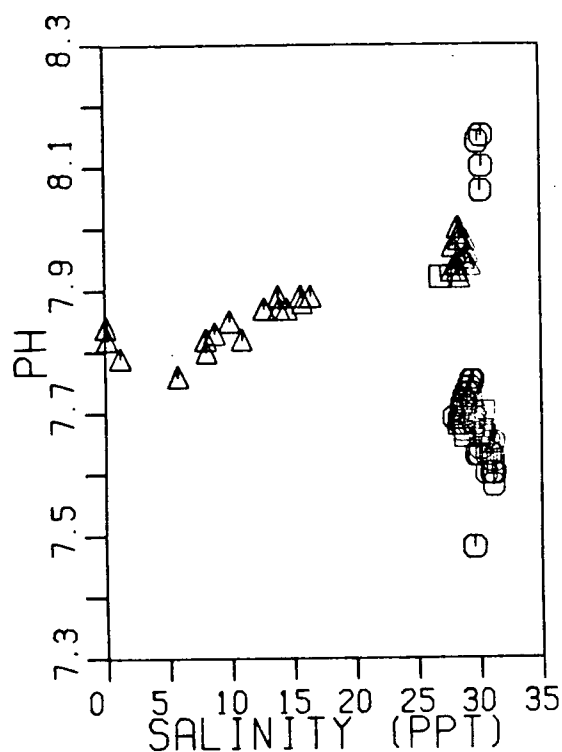


Figure 8c Cruise 79-01

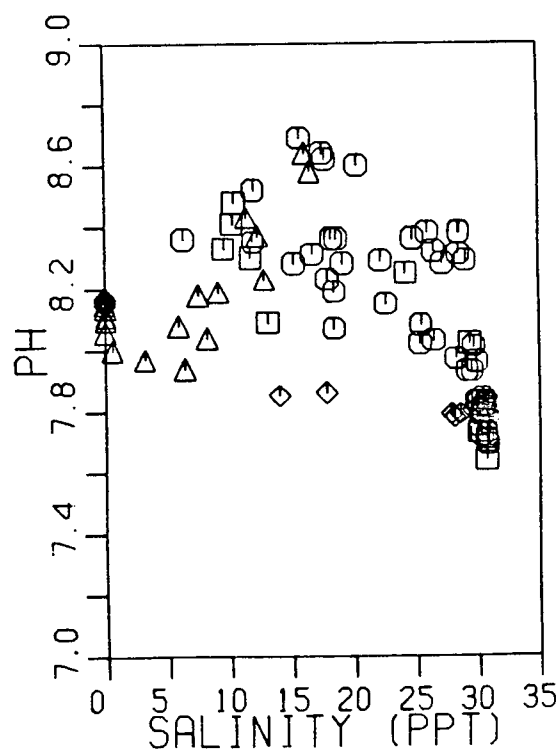


Figure 8d Cruise 79-12

FIGURE 8 pH data plotted versus salinity for Cruises 78-04, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

immediate vicinity of Sand Heads even though salinities are comparable. Unfortunately no pH data for salt wedge waters are available for this month.

The data for May 1979 (Cruise 79-12, Figure 8d), when samples were collected throughout the Strait of Georgia, are considerably more scattered. The pH minimum is again apparent for surface estuarine waters at a salinity near 5 ppt. River water seems to be homogeneous top to bottom with respect to pH. Very few data are available for estuarine bottom waters; however, the pH is lower for salt wedge water than for surface water of a corresponding salinity. As a general observation, pH values were higher, both in the Fraser River and Strait of Georgia, than at any other time of the year. Measurement through the water column indicated a decrease of pH with depth.

3.3 Discussion

3.3.1 Distribution of Alkalinity

While conservative behaviour of alkalinity has been observed in the Columbia (Park et al., 1972) and St. Lawrence Estuaries (Pelletier and Lebel, 1979; Lebel and Pelletier, 1980), Wong (1979) found a more complex relationship between alkalinity and salinity in the James River. Here, the alkalinity was nearly constant below a salinity of 5 ppt but then increased linearly with salinity. The alkalinity/salinity relationship in the Fraser River is similarly complicated.

Wong (1979) attributed the apparent non-conservative behaviour observed at low salinities to either removal of

alkalinity or the mixing of fresh water from various sources. In examining the Fraser Estuary, a number of possibilities exist to explain the anomalous behaviour of alkalinity. Points to consider include:

- (1) error of the method at low salinities
- (2) removal of alkalinity at low salinities
- (3) mixing of water from various sources

Errors in alkalinity determinations at low salinities must be considered since these measurements were made outside the range for which the technique of Anderson and Robinson (1946) has been standardised. The computation of alkalinity requires knowledge of the hydrogen ion activity coefficient, f_{H^+} , which varies with salinity. Values for f_{H^+} were taken from Anderson and Robinson (1946); however, at very low salinities f_{H^+} was assumed to approach 1.0 as the salinity approached 0.0 ppt and f_{H^+} may be overestimated in this manner. Considering Cruises 78-04 and 78-16, f_{H^+} would have to be 0.913 and 0.885, respectively, in order to alter fresh water alkalinities such that recalculated values corresponded to the 0.0 ppt intercept of the alkalinity/salinity relationship.

For comparative purposes, the alkalinity of a Fraser River water sample was determined by the method of Anderson and Robinson (1946) and using a Gran titration procedure (Gieskes and Rogers, 1973). Mean values for duplicate analyses by each method were 0.88 and 0.78 meq/l respectively suggesting that the former procedure may overestimate the alkalinity by approximately 0.1 meq/l. However, measured alkalinities may be more than 0.1 meq/l greater than the 0.0 ppt intercept (Figures

6b and 6d). Also, the value for f_{H^+} required to give agreement between the two techniques is 0.946. Nevertheless, this exceeds the calculated f_{H^+} values required for alkalinities at low salinities to conform to a linear relationship.

The apparent non-conservative behaviour of alkalinity at low salinity is interpreted to be real rather than an artifact of the methodology. However, bearing in mind the limitations of the data, alkalinity losses in the Fraser Estuary (Figure 6) may be exaggerated since fresh water alkalinities may be overestimated.

Wong (1979) considered removal of carbonate alkalinity at low salinities by calcite precipitation as an explanation for non-conservative behaviour. Calculations by Mook and Koene (1975) and Lebel and Pelletier (1980) indicate that supersaturation of estuarine waters with respect to calcite should not occur until relatively high salinities are attained. Moreover, Garrison et al. (1969) estimated that the Fraser River was undersaturated with respect to calcite by at least an order of magnitude. Taking these observations into account, carbonate precipitation seems an unlikely explanation for anomalous alkalinities in the initial mixing zone.

There are several non-carbonate components of the titration alkalinity, some of which may be removed rapidly as the ionic strength starts to increase. Hoos and Packman (1974) list several pollutants which are introduced into the Fraser River and Estuary and which may be responsible for the non-conservative behaviour of the alkalinity. Laundry establishments discharge boron wastes while organic compounds

with titratable functional groups may be found in the effluents from several industries, especially the wood products industry. While boron has been shown to behave non-conservatively in estuaries (Liss and Pointon, 1972), the fate of the organic material during estuarine mixing is less certain. In all cases, however, the concentrations of these materials necessary to affect the alkalinity would have to be excessively great.

Suspended sediments may be considered since alkalinity measurements were performed on unfiltered waters. Alkalinity attributable to the suspended sediment load would exhibit non-conservative behaviour because the total suspended particulate concentration decreases rapidly with increasing salinity. Two possible sedimentary contributions must be examined. Firstly, clay minerals have ion-exchange sites (Garrels, 1965; Siever, 1968) which may act as proton acceptors when water samples are acidified to determine alkalinity. This would cause an overestimation of alkalinity. While cation exchange capacities for Fraser River sediments were not measured in this study, Pharo (1972) reported values ranging from 6.73 to 8.29 meq/100g. Also, Kennedy (1965), cited by Sayles and Mangelsdorf (1977), reported total exchange capacities for American rivers ranging from 5.6 to 47.4 meq/100g. Considering a suspended sediment load of 20 mg/l, the maximum fresh water concentration measured in October 1978, and assuming a maximum cation exchange capacity of 50 meq/100g; this gives a cation exchange capacity of only 1×10^{-2} meq/l for the Fraser River, insufficient to account for the alkalinity anomaly. Secondly, any carbonate present in the suspended load may contribute to

the titration alkalinity. However, the concentration of carbonate material in the particulate material is unknown.

Mixing of water from various sources could generate the observed alkalinity/salinity relationship and several models could be hypothesized. Firstly, the major fresh water input is the Fraser River itself but a number of sewage outlets and storm drains discharge into the estuary. However, the non-conservative behaviour of alkalinity appears to be related to salinity only, with no discernable geographic influences. Secondly, as evident in October 1978, the river water alkalinity is subject to short term fluctuations. If the residence time of water in the upper reaches of the estuary is sufficiently long, the behaviour of alkalinity may be a manifestation of complex mixing of river waters with varying alkalinity. This would seem unlikely since measured fresh water alkalinities were always higher than predicted by extrapolation of conservative behaviour to the river water end member. Thirdly, data for October 1978 (Figure 6c) can be interpreted as two intersecting linear relationships. Variations in fresh water input would alter the slope of the initial mixing curve as well as the point of intersection of the two linear relationships. For example, intersection points near salinities of 7 and 14 ppt are observed for dilution curves with end members having fresh water alkalinities less than 1 meq/l and greater than 1 meq/l respectively. However, the alkalinity data do not indicate what processes may establish different conservative mixing curves for the low and high salinity ranges.

3.3.2 Distribution of Dissolved Oxygen

Data from the Strait of Georgia illustrate the influence of biological processes on the concentration of dissolved oxygen in natural waters. Concentrations tend to decrease below the surface due to the oxidation of organic matter. The percentage oxygen saturation during Cruise 78-16 was calculated using expressions from Weiss (1970). While fresh water samples from all depths were 100% saturated with oxygen, levels fell to 55% saturation in bottom waters of Station 15.

Samples from 1 and 5m depths at Station 15 were supersaturated with respect to oxygen, thereby indicating photosynthetic activity. This accounted for the slight departure from conservative behaviour for surface waters in the lower reaches of the estuary (Figure 7b). Similarly, the scatter exhibited by data during the freshet (Figure 7d) resulted from intense primary production.

Except during the freshet, the dissolved oxygen behaves conservatively in the surface waters of the Fraser Estuary (Figure 7). Variations in the oxygen content of river water result from the temperature dependence of the solubility. Although the bottom waters in the estuary may be undersaturated with respect to oxygen, data from Cruise 78-16 (Figure 7b) indicate that dissolved oxygen also behaves conservatively in the salt wedge at salinities less than 27 ppt. Thus, primary production in the Fraser Estuary is minimal, except during the summer, and there is no evidence of biological utilization of oxygen in the salt wedge.

3.3.3 Distribution of pH

The distribution of pH in the Fraser estuary and Strait of Georgia exhibits a number of general features regardless of the sampling time. Four distinct trends which will be discussed separately are:

- (1) depth-related pH variations
- (2) pH distribution in the surface waters of the Strait of Georgia
- (3) pH distribution in the surface waters of the Fraser estuary
- (4) pH in the salt wedge

The pH profile at Station 15 in October 1978 (Figure 9) illustrates the observations mentioned in Section 3.2.3 that there are low pH values below the surface. The decrease of pH with depth was consistent in the Strait of Georgia at all stations throughout the year and reflects biological influences, that is, the in situ generation of carbon dioxide which depresses the pH of the water.

The pH of surface waters in the Strait of Georgia shows seasonal variations related both to primary productivity and mixing processes. The uniformly low pH values observed in January 1979 (Figure 8c) occur because winter mixing brings high salinity, low pH water to the surface. In May 1979 (Figure 8d) the pH values are higher than measured at any other time of year and agree with those of Tully and Dodimead (1957). Their observed maxima, pH 8.8, occurred in areas associated with high oxygen and phytoplankton concentrations. High primary productivity at this time depresses the carbon dioxide

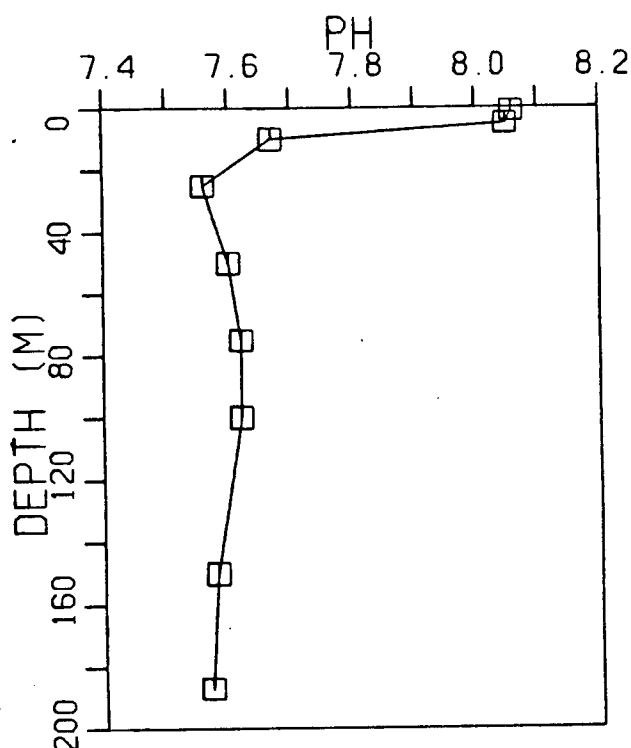


FIGURE 9 The pH profile at Station 15, Cruise 78-16.

concentration but elevates the pH. Patchy biological activity coupled with complex mixing patterns in the Strait of Georgia leads to an incoherent distribution of surface pH; hence the apparent scatter in the dissolved oxygen and pH data with respect to salinity.

A distinct pH minimum in the surface waters of the Fraser Estuary was observed during all four estuarine cruises. Because there are more data available from Cruise 78-16, data from October 1978 will be examined in detail in order to elucidate features common at all times.

As illustrated in Figure 8b, the mixing of surface waters from the Fraser River (with a mean pH of 7.85) and the Strait of Georgia (with a pH of 8.06) resulted in a pH minimum of 7.72 at a salinity of 1.5 ppt. Such a situation has been observed in the Tamar, Scheldt and Rhine estuaries (Mook and Koene, 1975;

Morris et al., 1978; Wollast et al., 1979) and attributed either to variations in the carbonic acid dissociation constant or to biological processes.

In order to investigate the origin of the pH minimum, the model of Mook and Koene (1975) was used to establish theoretical dilution curves for pH which were then compared with field data from the Fraser River. As discussed in Section 3.1, the model computes the pH at any salinity from carbonate equilibria. Alkalinity and total inorganic carbon are treated as conservative properties. The salinity, alkalinity and pH of two end members are required and the system is considered to be isothermal.

Although the discussion of alkalinity in Section 3.3.1 indicates that these conditions may not be met in the Fraser Estuary, the model of Mook and Koene (1975) does provide a starting point for the analysis of the pH data. Considering first of all the surface waters, two end members for river water and one for sea water were used to generate the dilution curves in Figure 10. These are meant to represent ideal mixing processes for surface waters. Samples with a salinity less than 1.0 ppt were divided into two subsets characterized by alkalinity, either less than or greater than 1.0 meq/l. The properties of the fresh water end members were then defined by taking the mean alkalinity and pH of all samples in each data subset. Sea water properties were defined by samples collected near Sand Heads. Comparison with field data indicated that the trend for calculated pH in the surface waters mimics measured values except that the minimum occurs at a higher pH and lower

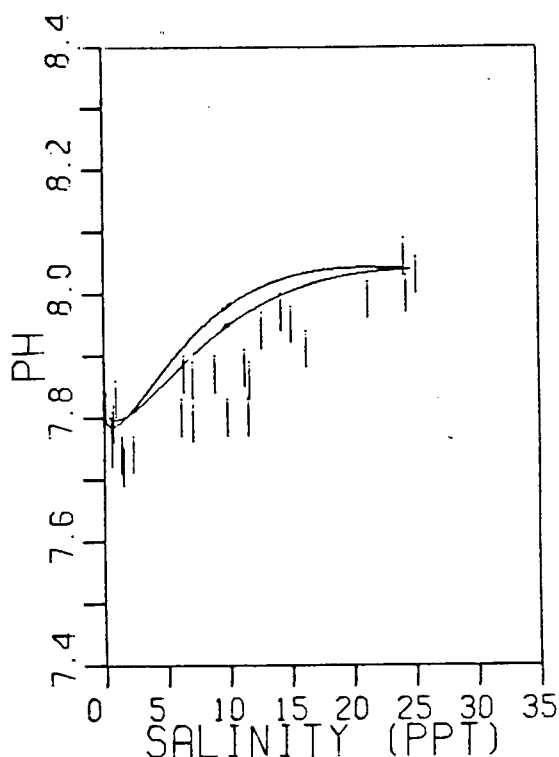


FIGURE 10 The theoretical dilution curve for pH in surface waters of the Fraser Estuary generated by considering a single step mixing of one sea water and two river water end members. Data for the water properties of the end members are taken from Cruise 78-16. Fresh water end members: sal 0 ppt, alk 0.87 meq/l, pH 7.82; sal 0 ppt, alk 1.07 meq/l, pH 7.84. Sea water end member: sal 24.787 ppt, alk 1.85 meq/l, pH 8.04. Temp=12.5°C. Vertical lines represent measured pH values ± 0.03 pH units.

salinity than actually observed.

Adjustments of the model were made in attempts to improve the approximation with measured pH values. Some success was achieved by considering the estuarine mixing as a two step process. An intermediate water mass was defined with a salinity of 7 ppt, alkalinity of 1.09 meq/l, and pH of 7.83. The dilution curve in Figure 11 represents mixing of this intermediate end member with both river and sea water. Theoretical pH calculations generated in this manner more closely agree with measured values than did those resulting from

a single stage dilution. However, the minimum is still not developed as extensively as observed in the estuary.

Further amplification of the pH minimum due to the types of biological processes proposed by Morris et al. (1978) seems unlikely. The dissolved oxygen data presented in Figure 7b indicated no sudden concentration decrease in the surface waters at low salinity. On the contrary, conservative behaviour was observed and the surface waters throughout the estuary exhibited oxygen saturation levels near 100%. Minimal primary productivity, as anticipated in October, would be necessary for total inorganic carbon to be conservative, and hence the successful application of the model. This may account for the reasonable agreement between the theoretical and observed pH values.

The model was also used to examine pH in estuarine surface waters in January 1979. The dilution curves (Figure 12) generated by mixing Fraser River water with three different marine end members developed pH minima but could not replicate measured values. Since biological activity at this time would have been minimal, the lack of accord again suggests a mixing pattern more complex than a single step dilution of sea water.

The bottom waters in the Fraser Estuary exhibit two features which distinguish them from surface waters (Figure 8). Firstly, the pH is lower than observed in surface waters of a comparable salinity. Since the bottom waters are undersaturated with respect to oxygen by 10 to 20%, this indicates that biologically produced carbon dioxide must decrease the pH. However, the oxygen deficit could have been generated outside

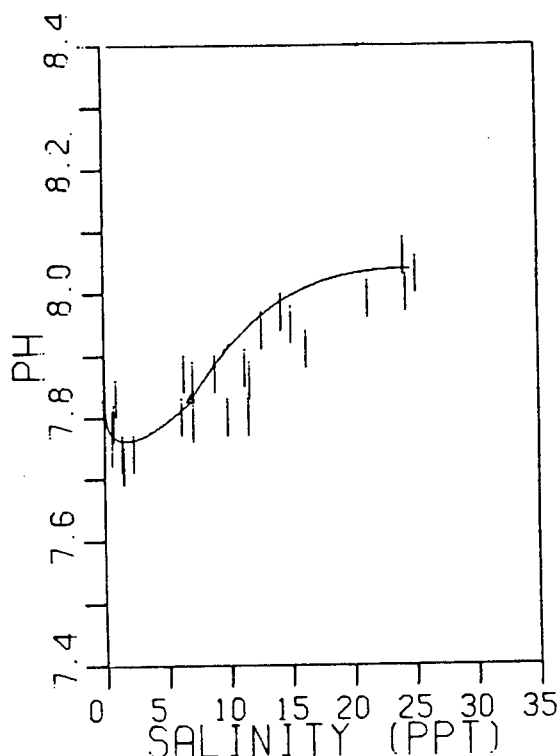


FIGURE 11 The theoretical dilution curve for pH in surface waters of the Fraser Estuary generated by considering the mixing as a two step process. Data for the water properties of the end members and intermediate water mass are taken from Cruise 78-16. Fresh water end member: sal 0 ppt, alk 1.07 meq/l, pH 7.84; Intermediate water body: sal 7.000 ppt, alk 1.09 meq/l, pH 7.83; Sea water end member: sal 24.787 ppt, alk 1.85 meq/l, pH 8.04. Temp=12.5°C. Vertical lines represent measured pH values ± 0.03 pH units.

the estuary. Secondly, the pH remains relatively uniform regardless of the salinity. This is evident particularly in October 1978 and to some extent in May 1979. Because these measurements are associated with the resuspension of large quantities of bottom sediments, the pH may be influenced by a localized geochemical buffering system due to ion-exchange reactions with clay minerals. The model of Mook and Koene (1975) was used to determine the extent to which mixing processes alone could affect the pH.

There are difficulties in defining an appropriate sea water end member and in comparing the calculated pH results with field

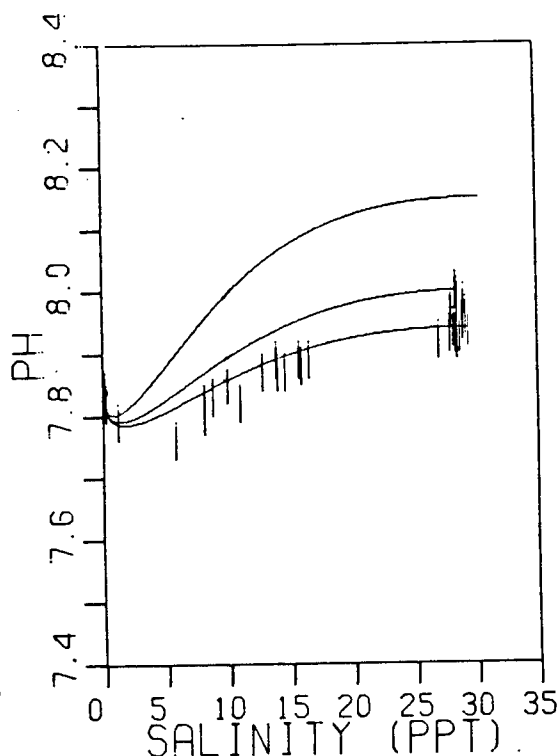


FIGURE 12 The theoretical dilution curve for pH in surface waters of the Fraser Estuary generated by considering a single step mixing of fresh water with three sea water end members. Data for the water properties of the end members are taken from Cruise 79-01. Fresh water end member: sal 0 ppt, alk 1.15 meq/l, pH 7.84; sea water end members: sal 30.315 ppt, alk 2.11 meq/l, pH 8.15; sal 28.386 ppt, alk 2.04 meq/l, pH 8.00; sal 29.407 ppt, alk 2.07 meq/l, pH 7.94. Temp=6.0°C. Vertical lines represent measured pH values ± 0.03 pH units.

data. The pH data were collected on different days at various sites in the Fraser Estuary and hence may not represent a discrete dilution curve. The theoretical pH values shown in Figure 13 represent possible ideal mixing curves in the estuarine bottom waters. Samples from Cruise 78-16 were used to define water properties of a single river end member together with four saline end members.

Theoretical results generated by mixing river water with the highest salinity end member bear no resemblance to the observed pH values. However, this is to be anticipated since the saline water properties were defined by bottom water (196m)

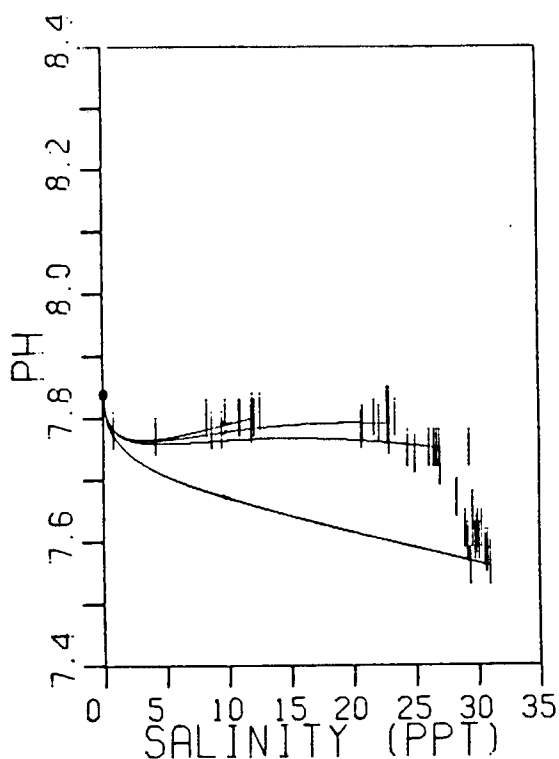


FIGURE 13 The theoretical dilution curve for pH in the salt wedge of the Fraser Estuary generated by considering a single step mixing of one fresh water and four sea water end members. Data for the water properties of the end members are taken from Cruise 78-16. Fresh water end member: sal 0 ppt, alk 1.09 meq/l, pH 7.84. Sea water end members: sal 12.114 ppt, alk 1.32 meq/l, pH 7.80; sal 22.901 ppt, alk 1.72 meq/l, pH 7.79; sal 26.740 ppt, alk 1.93, pH 7.75; sal 30.968, alk 2.16, pH 7.56. Temp=12.5°C. Vertical lines represent measured pH values ± 0.03 pH units.

from Station 15. The remaining curves better approximate the field data. In these cases, the saline end members were defined by salt wedge samples with varying salinities representing possible stages in the dilution curve for bottom waters. The most important feature is the uniformity of the calculated pH over most of the salinity range.

For cases in Figure 13, biological processes in the Strait of Georgia cause the low pH of the saline end member. Since the dissolved oxygen apparently behaves conservatively in the salt wedge (Figure 7b), the oxygen undersaturation calculated for

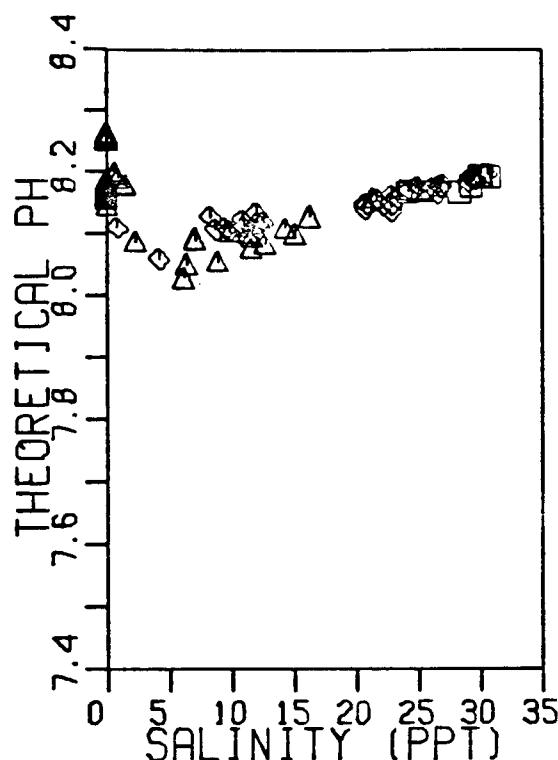


FIGURE 14 Theoretical pH values calculated from the alkalinity and assuming that the carbon dioxide was 100% saturated. Symbols: □ data at all depths for Station 15; △ surface samples in the Fraser Estuary; ◇ bottom samples in the Fraser Estuary.

these waters must result from the advection of oxygen-depleted water from outside the estuary. In situ production of carbon dioxide is insignificant and the total inorganic carbon content behaves conservatively. Thus, the pH of the salt wedge water may be explained by conservative mixing without invoking geochemical buffering effects.

A second method of calculating the pH of the estuarine waters was examined. The theoretical pH can be determined from the alkalinity assuming that carbon dioxide is 100% saturated at each point in the estuary. This establishes the total inorganic carbon content at each point removing the prerequisite of conservative behaviour. Carbon dioxide saturation was calculated using the expressions of Skirrow (1975) and the

resulting pH calculations for Cruise 78-16 are shown in Figure 14. In all cases, theoretical pH values were higher than observed values indicating that this procedure underestimates the carbon dioxide concentrations. Carbon dioxide levels calculated from the alkalinity and pH were supersaturated by a factor of 1.3 to 4.1. This indicates that carbon dioxide either produced in situ or advected from outside the estuary does not evade to the atmosphere from the estuarine waters at a rate fast enough for these waters to attain equilibration with the atmospheric carbon dioxide concentration.

3.4 Summary

Throughout the year, the alkalinity exhibits conservative behaviour through most of the salinity range. Deviations from this linear relationship are evident at low salinities. To a certain extent these alkalinity anomalies may be attributed to an overestimation of the alkalinity of low salinity samples; however, the possibility of alkalinity removal cannot be ignored. Alternatively, data from Cruise 78-16 (Figure 6c) can be interpreted as two intersecting linear relationships.

Except during the freshet, the dissolved oxygen also behaves conservatively in the Fraser Estuary. The oxygen undersaturation calculated for salt wedge waters results from the horizontal advection of oxygen depleted water from outside the estuary. Only during the summer months is the concentration of dissolved oxygen in estuarine waters modified by biological processes.

Throughout the year surface waters of the Fraser Estuary

exhibited a pronounced pH minimum at low salinity. This cannot be replicated theoretically by considering a simple single stage dilution; however, a two step dilution involving an intermediate water mass gives reasonable agreement with observed pH values. Bottom waters throughout the salt wedge have a low and relatively uniform pH. These pH values can be explained by the advection and subsequent mixing of oxygen-depleted water from outside the estuary. The pH of sea water in the Strait of Georgia, both at depth and at the surface, is influenced by biological processes.

Postulating the formation of an intermediate water mass facilitates the explanation of observed alkalinity and pH measurements in the surface waters of the Fraser Estuary. This water mass must be formed by mixing salt wedge and river water. Discrete water properties can be attained only if sea water entering the estuary via the salt wedge becomes modified prior to vertical advection. The consequences of such a process on manganese chemistry will be examined in the following chapter.

4. MANGANESE DISTRIBUTION IN THE FRASER ESTUARY

4.1 Preamble

The Fraser Estuary was investigated five times under varying flow regimes (see Section 2.1.1). Data for dissolved and particulate manganese are tabulated in Appendices B.1 and B.2, respectively.

While this chapter deals primarily with the chemistry of manganese in the Fraser Estuary, data for total suspended particulate concentrations and particulate aluminium concentrations are included since they are useful in explaining some features of manganese behaviour.

4.2 Field Data: Aqueous Samples

4.2.1 Dissolved Manganese

Dissolved manganese concentrations in estuarine waters, plotted versus salinity, are shown in Figures 15a through 15d for Cruises 78-04, 78-16, 79-01, and 79-12, respectively. Figures 15c and 15d include data collected throughout the Strait of Georgia. These data will be discussed in greater detail in Chapter 5 which deals with the temporal and spatial distribution of manganese in the strait.

In March 1978 (Cruise 78-04, Figure 15a) the dissolved manganese concentration in the river water was in the range 9.97 to 13.0 ppb, concentrations in the bottom waters being somewhat higher than those in the surface waters. Strait of Georgia

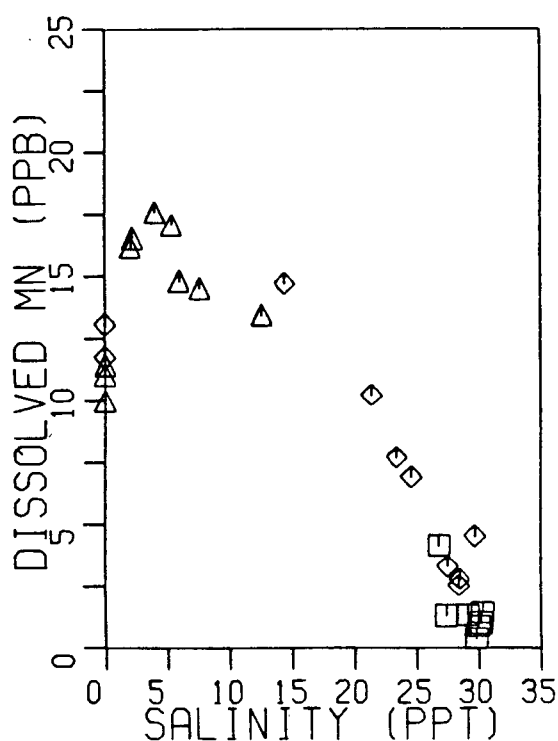


Figure 15a Cruise 78-04

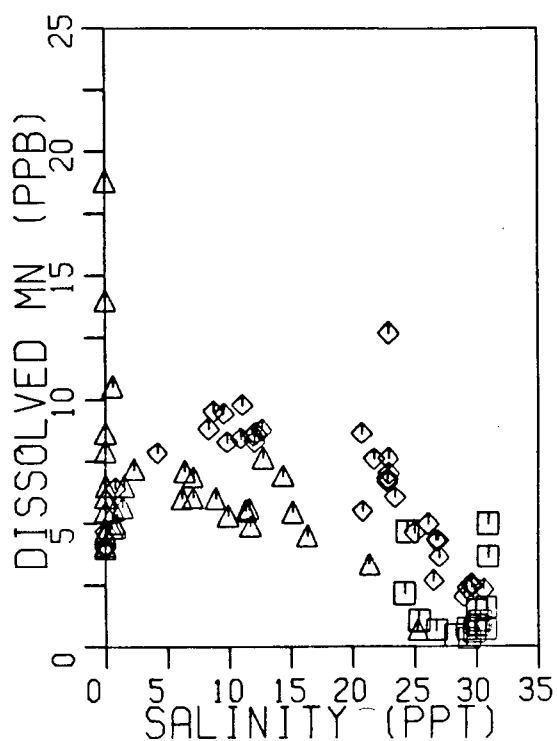


Figure 15b Cruise 78-16

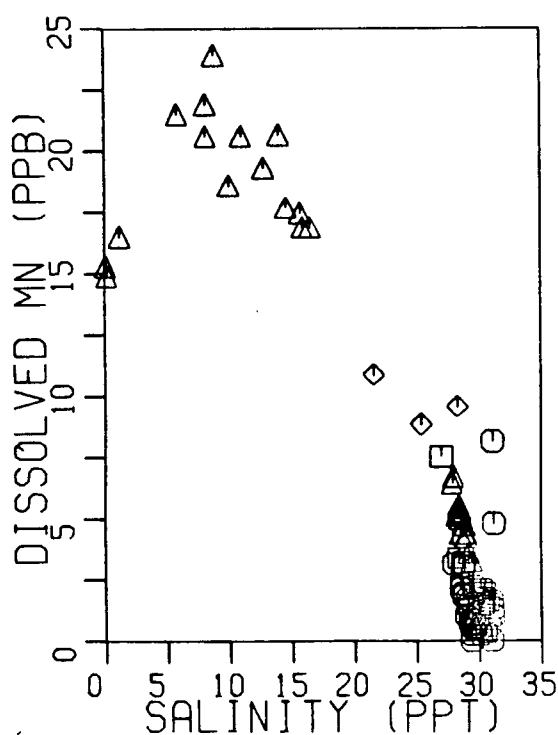


Figure 15c Cruise 79-01

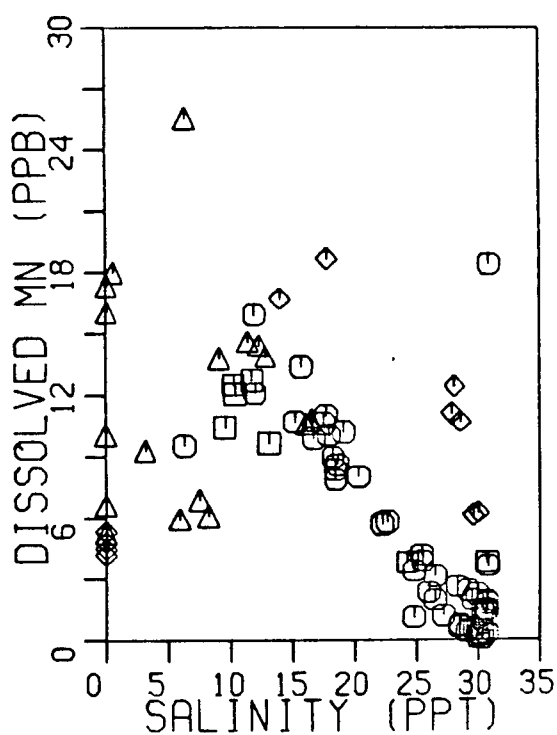


Figure 15d Cruise 79-12

FIGURE 15 Dissolved manganese data plotted versus salinity for Cruises 78-04, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

samples, as exemplified by Station 15, exhibited a surface concentration of 4.12 ppb (salinity 26.837 ppt) which decreased to a mid-depth minimum of 0.37 ppb. Estuarine samples from both the surface and bottom followed a similar dilution pattern although, in both cases, the sample series were incomplete with respect to the salinity range in the estuary. A maximum dissolved manganese concentration of 17.6 ppb was evident in the surface waters at a salinity of 4.028 ppt.

Very few data are available for Cruise 78-11. (See Appendix B for data). Fraser river concentrations were in the range 1.97 to 2.93 ppb. Estuarine bottom waters exhibited dissolved manganese levels which increased with salinity. It should be noted that the samples were collected on a flooding tide.

During the week prior to the three day cruise in the Fraser Estuary in October 1978 (Cruise 78-16), a series of samples was collected daily at Fort Langley (Figure 2). These data are recorded sequentially in Appendices B.1 and B.2 as Station 70, Cruise 78-16. During this time period dissolved manganese concentrations fell from 18.8 ppb to 4.45 ppb, a value more typical of those observed in the Fraser River during the cruise (Figure 15b). Surface estuarine waters exhibited a mixing pattern similar to that seen in March. That is, dissolved manganese concentrations were greatest at low salinities. Surface waters exhibited two dissolved manganese maxima, a reflection of sampling on different days. Bottom samples collected during a time series at Anchor Station 56.3 (Appendix B.3) showed that the dissolved manganese concentrations ranged

from 2 to 5 ppb in high salinity samples (26 to 27 ppt) but varied from 8 to 10 ppb in the low salinity samples (8 to 12 ppt) which were collected from the toe of the salt wedge at low water slack. Data from another station, 58.3, upstream of 56.3 but situated in a small basin, indicate that salinities remained as high as 23 ppt during low water slack and dissolved manganese ranged from 6.03 to 7.58 ppb. A complete depth profile was obtained at Station 15 on both the first and last day of the cruise. While absolute concentrations varied from one day to the next, a persistent profile was observed on each occasion. Concentrations near 4 ppb in surface waters dropped to a minimum near 0.5 ppb at mid-depth but increased near the bottom to levels in the range 3.6 to 4.9 ppb. Data from Station 15 are discussed in detail in Chapter 5.

Data in January 1979 (Cruise 79-01, Figure 15c) mimic the trend observed in March 1978 with the exception that the dissolved manganese content in the river water and at the maximum was higher by 5 ppb in January.

Data from Cruise 79-12 (Figure 15d) followed the same trend exhibited at other times of the year, with the exception of four samples from Station 53 (Appendix B.2). Three samples were riverine with dissolved manganese concentrations ranging from 16.1 to 18.0 ppb. The fourth sample had a salinity of 6.412 ppt and a dissolved manganese content of 25.6 ppb. In all cases, the dissolved manganese concentrations were anomalously high, exceeding values exhibited by surface waters of comparable salinity collected at other stations. Also, these samples were associated with high suspended sediment loads relative to

surface waters collected elsewhere. Considering the remainder of the data from Cruise 79-12, dissolved manganese concentrations in Fraser River water mainly clustered around 5 ppb. The dissolved manganese maximum in the surface estuarine waters was observed at a salinity near 12 ppt. The few bottom samples collected exhibited concentrations higher than did surface waters of a comparable salinity.

4.2.2 Particulate Manganese

Particulate manganese concentrations, plotted versus salinity, are depicted in Figures 16a through 16d for Cruises 78-04, 78-16, 79-01 and 79-12, respectively. Although absolute concentrations vary from one cruise to the next, a reflection of the differing discharge rates, a number of features are evident on all occasions. The few data from Cruise 78-11 are also consistent with these observations which include:

- (1) the particulate manganese concentration in the Fraser River end member varies considerably
- (2) estuarine surface samples follow a smooth dilution curve, concentrations decreasing either linearly or exponentially with salinity depending upon the cruise.
- (3) bottom samples exhibit very high concentrations which are independent of both salinity and station location.

One sample from Cruise 78-04, with a salinity near 25 ppt, is presumed to reflect a sampling error. That is, the bottom water sampler may not have tripped until it lay on the bottom,

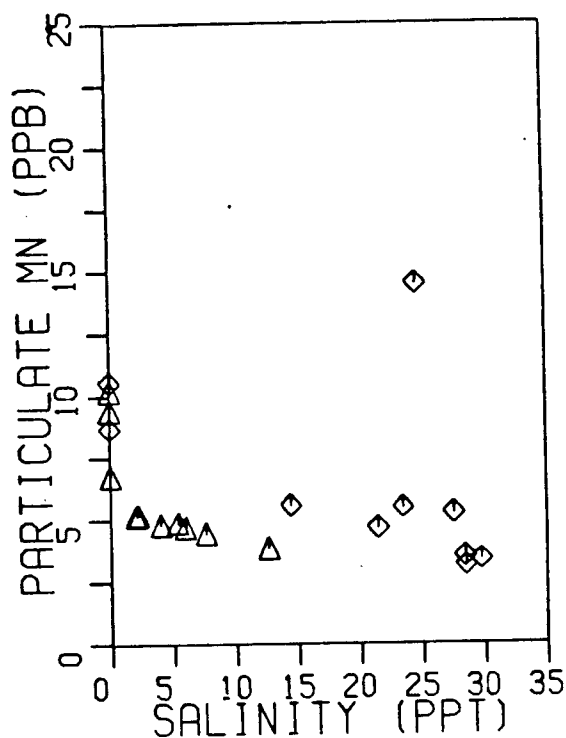


Figure 16a Cruise 78-04

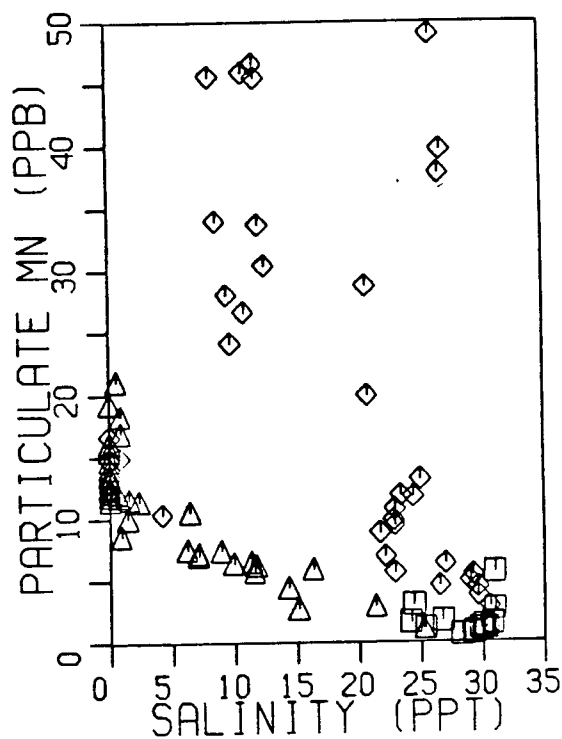


Figure 16b Cruise 78-16

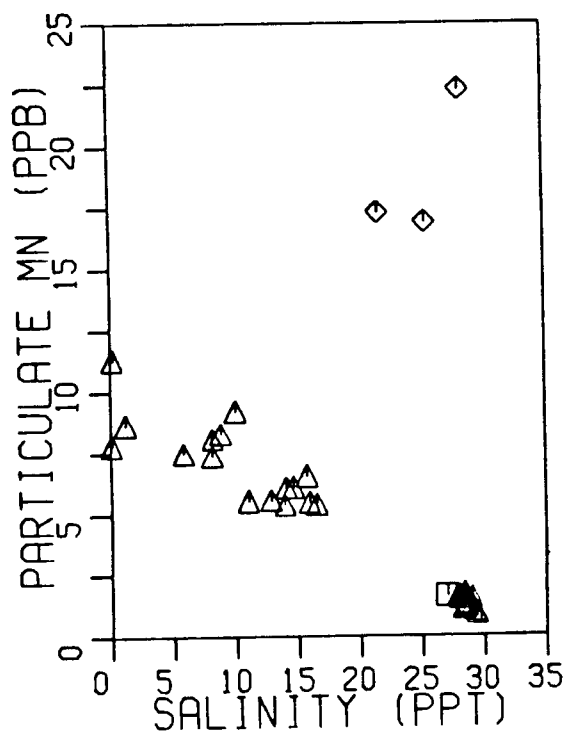


Figure 16c Cruise 79-01

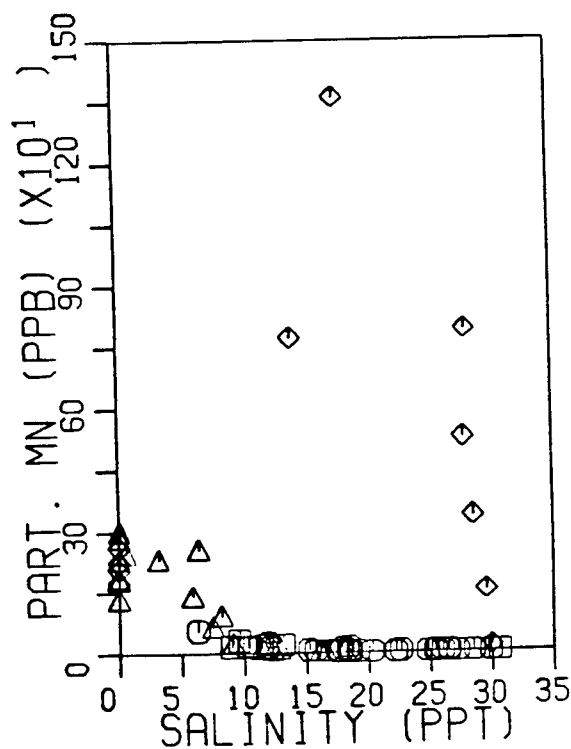


Figure 16d Cruise 79-12

FIGURE 16 Particulate manganese data plotted versus salinity for Cruises 78-04, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Straits of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

thereby collecting bedload as well as suspended sediments.

4.2.3 Particulate Aluminium

Particulate aluminium concentrations, plotted versus salinity, are shown in Figures 17a through 17d for Cruises 78-04, 78-16 79-01, and 79-12, respectively. Although concentrations are generally two orders of magnitude higher, the distribution of particulate aluminium displays features similar to the distribution of particulate manganese.

There is considerable variation in the particulate aluminium concentration of both Fraser River and estuarine bottom water samples. In contrast, estuarine surface samples follow the linear or exponential decreases in concentrations evident for particulate manganese.

4.2.4 Total Suspended Particulates

Total suspended particulate concentrations were measured during Cruises 78-16 and 79-12. The results, plotted versus salinity, are presented in Figures 18a and 18b, respectively. Again the data follow trends evident for the particulate metals.

Concentrations in the Fraser River ranged from 11.1 to 24.1 mg/l in October 1978 and from 186 to 540 mg/l in the following May. On both occasions the suspended sediment load in estuarine surface waters decreased rapidly in the initial mixing zone. Estuarine bottom waters exhibited high concentrations of suspended material which were related to neither the salinity nor the station location.

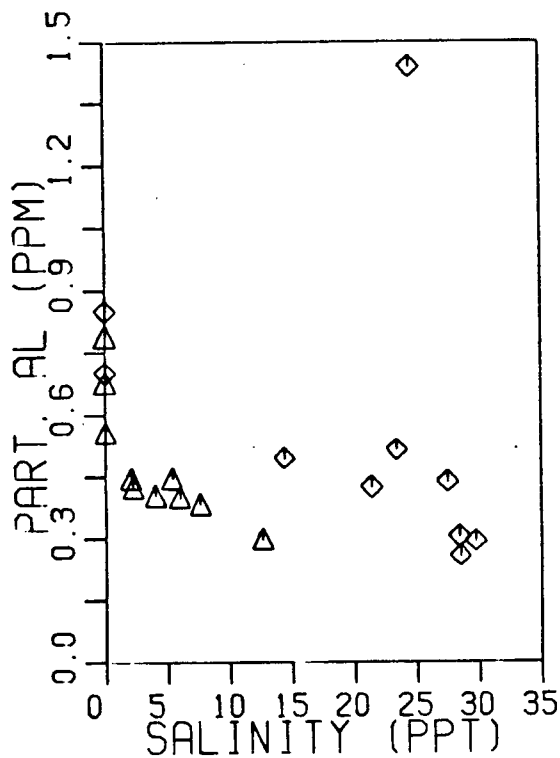


Figure 17a Cruise 78-04

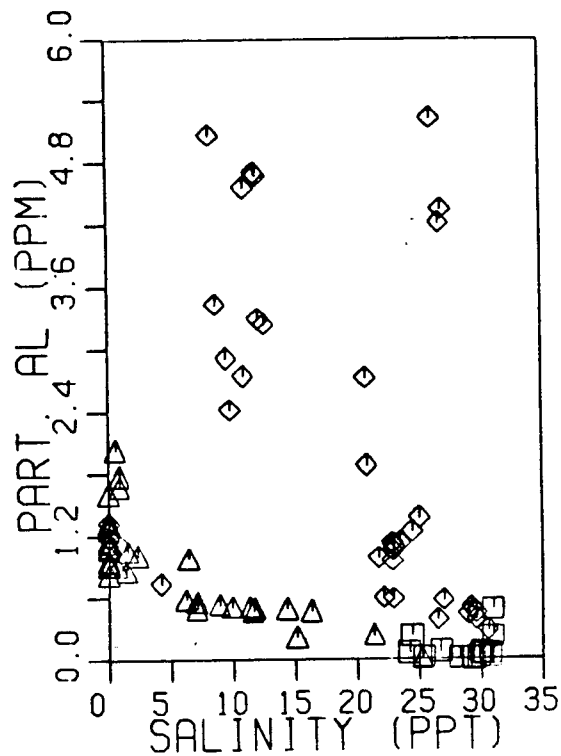


Figure 17b Cruise 78-16

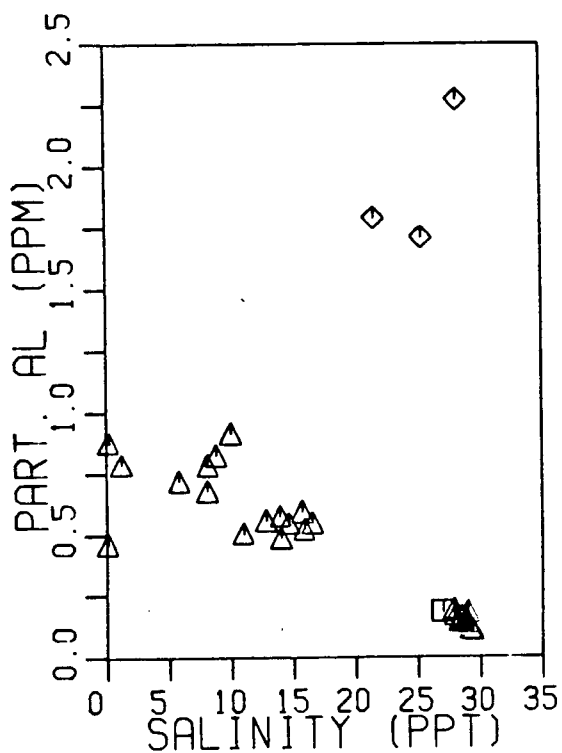


Figure 17c Cruise 79-01

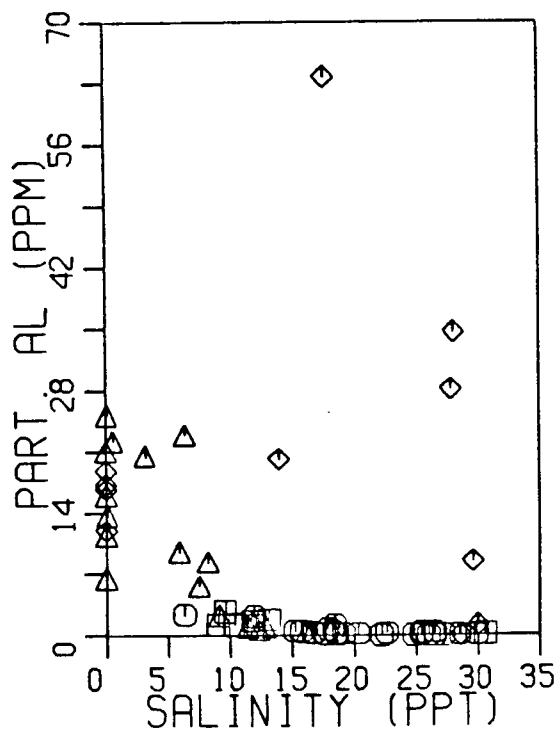


Figure 17d Cruise 79-12

FIGURE 17 Particulate aluminium data plotted versus salinity for Cruises 78-04, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Straits of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

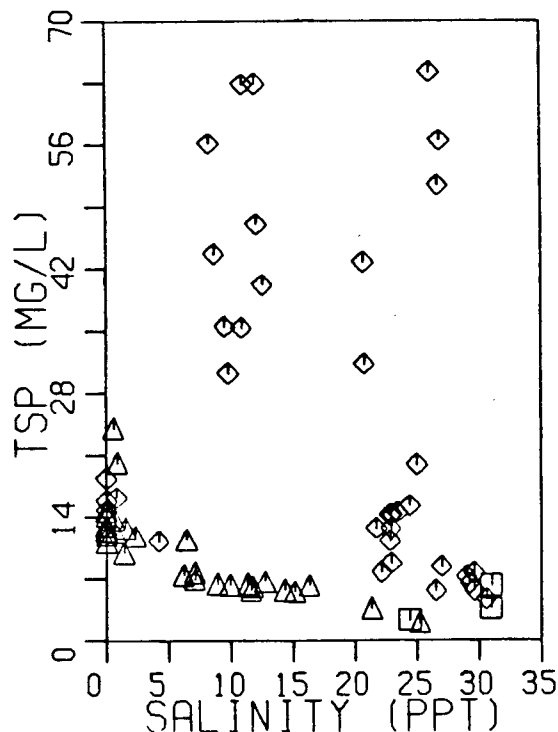


Figure 18a Cruise 78-16

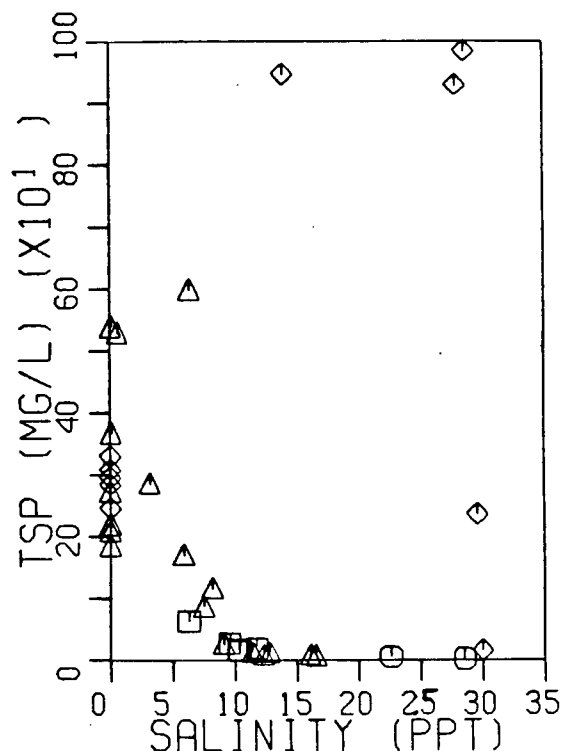


Figure 18b Cruise 79-12

FIGURE 18 Total suspended particulate concentrations plotted versus salinity for Cruises 78-16 and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Straits of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

4.3 Field Data: Sediments

4.3.1 Interstitial Water

Interstitial water was extracted from cores collected at Station 15 and various sites in the Fraser Estuary. The dissolved manganese concentrations and salinities in the interstitial waters of the estuarine sediments are presented in Appendix C.

The dissolved manganese profile in the interstitial water was similar in two cores collected at Station 15 (Appendix C.1). A subsurface maximum of 3.85 and 4.81 ppm, for cores 78-1-15 and

79-2-15, respectively, was observed in the 3 to 6 cm section. The concentration decreased regularly with depth and was approximately 1 ppm near the bottom of the 50 cm cores.

In comparison with river and sea water samples, interstitial waters from estuarine sediments exhibited dissolved manganese enrichment. Cores collected by divers in February 1979 from three stations in the lower reaches of the Fraser Estuary displayed different dissolved manganese profiles (Appendix C.2). Sediments from Station 56.2 displayed two subsurface maxima: 10.9 ppm at 6 to 9 cm and 6.30 ppm at 19 to 22 cm. Interstitial waters of sediments from Station 59.0 were enriched in dissolved manganese to an even greater degree. In comparison, the core from Station 57.2 was depleted in manganese at all depths, with a maximum concentration of only 126 ppb in the 6 to 9 cm section.

All but one estuarine core collected by divers in January 1980 exhibited relatively low dissolved manganese concentrations (Appendices C.4 and C.5). Interstitial waters of sediments from both Station 57.2 and Station 59 were depleted in manganese at this time. The exception, Station 56.2, again displayed two subsurface maxima: 4.4 ppm at 9 to 12 cm and 5.7 ppm at 24 to 27 cm.

The interstitial water salinity was measured for cores collected in 1980, primarily to determine whether the integrity of the core was preserved in the sampling process. The salinity profile in sediments from Station 67 indicates fresh water throughout the length of the core. In general, the salt content of interstitial waters increases downstream. However, the

salinity profile at some stations follows no regular trend and may display a subsurface minimum (Station 57.2, Appendix C.4; Station 56.2, Appendix C.5).

4.3.2 Ammonium Oxalate Digest

Sediments collected with a Shipek Grab during Cruise 79-12 and selected samples from cores obtained in January 1980 were subjected to an ammonium oxalate extraction. Results are presented in Appendices C.3 and C.5 respectively.

In May 1979, the concentration of ammonium oxalate extractable manganese generally decreased from 125 to 130 ppm in riverine surface sediments to values in the range of 70.8 to 74.0 ppm for marine surface sediments. Sediments at Station 53, with a concentration of 153 ppm, did not conform to this trend.

Surface sediments collected in January 1980 contained more extractable manganese than sediments collected in the previous May. The concentration in riverine sediments was 168 ppm at the surface and 150 to 156 ppm in subsurface layers. Sediments collected from Station 60.5, near the site of the furthest upstream advance of the salt wedge at this time, exhibited similar concentrations: 161 ppm at the surface and 133 ppm at depth. The profile of extractable manganese in sediments near Steveston (Station 56.2) showed a mid-depth maximum of 243 ppm with concentrations at the surface and bottom of the core (27 to 30 cm) of 80.2 and 81.9 ppm, respectively.

4.3.3 Total Acid Digest

Manganese and aluminium concentrations were determined in the ammonium oxalate resistant fraction of the sediments. These data are also compiled in Appendices C.3 and C.5.

The resistant manganese concentration in estuarine sediments collected in May 1979 varied from 350 to 519 ppm giving total manganese contents in the range of 468 to 591 ppm. No trend was evident but the lowest total manganese concentration was observed near Steveston. The residual aluminium content ranged from 5.03 to 5.48% at this time.

In January 1980, the residual manganese concentrations in surface sediments were fairly uniform at three sites (Stations 56.2, 60.5, and 67.0) in the estuary, ranging from 291 to 316 ppm. The resistant aluminium varied from 4.46 to 5.21%. At Station 56.2 the concentrations of both manganese and aluminium paralleled the oxalate extractable manganese profile.

As mentioned in Section 2.2.4, samples collected during Cruise 79-12 were also subjected to the total acid digestion without prior oxalate extraction. Manganese concentrations agreed with the sum of the oxalate leachable and resistant fractions; however, the aluminium concentrations were consistently higher than observed in only the oxalate resistant fraction. This indicates that the ammonium oxalate digestion extracts a significant proportion of the total aluminium. Accordingly, Mn:Al ratios obtained for samples subjected to oxalate extraction are overestimates and should be considered unlikely maximum values.

4.3.4 Grain Size

Grain size analyses were performed on estuarine sediments collected in May 1979 (Cruise 79-12) with a Shipek Grab and on selected core sections from sediments obtained by divers in January 1980. Tabulated in Appendix C.6 are the mean grain sizes and standard deviations together with the percentages of sand and mud, where mud refers to the material finer than 63 μm .

Both in January and May, the surface sediments in the Fraser River and Estuary were relatively uniform in terms of grain size. These sediments consisted almost entirely of sand, containing less than 1% mud. Surficial sediments from deeper locations (Stations 15 and 53) had a higher percentage of fine-grained material, especially the manganese-rich sediments from Station 53 which contained 10% mud.

Examination of the riverine and estuarine cores revealed that the sediments also varied little through the length of the core. The most seaward core, Station 56.2, was exceptional. Sediments at the surface and below 24 cm were similar to other estuarine sediments but the intervening layer contained a high percentage of mud.

4.4 Discussion

4.4.1 Distribution of Suspended Particulate Material

An understanding of the behaviour of suspended particulate material is necessary before the distribution of manganese in the Fraser Estuary can be examined in detail. This behaviour can be investigated by considering total suspended particulate concentrations. Alternatively, the concentration of particulate aluminium may be a useful indicator of terrigenous material, although, the aluminium content in the suspended material can vary with the mineralogical composition and grain size distribution of the suspended particulates (Spencer and Sachs, 1970; Price and Calvert, 1973; Sholkovitz and Price, 1980). Although dissolved aluminium precipitates from low salinity estuarine waters (Hydes and Liss, 1977), the contribution to the particulate concentration is negligible. Plots of particulate aluminium concentrations versus the suspended sediment load (Figure 19) suggests that particulate aluminium may be used as an indicator of terrigenous material in the Fraser Estuary during non-freshet months. According to Milliman (1980), this corresponds to periods when most of the sand fraction of the suspended sediment load is deposited in the upper reaches of the estuary, leaving primarily the silt and clay fraction in suspension.

The concentration of suspended material in river water shows a strong dependence on the discharge rates. In agreement with Milliman (1980), lowest values occur during minimal discharge in January and March while maximum values were

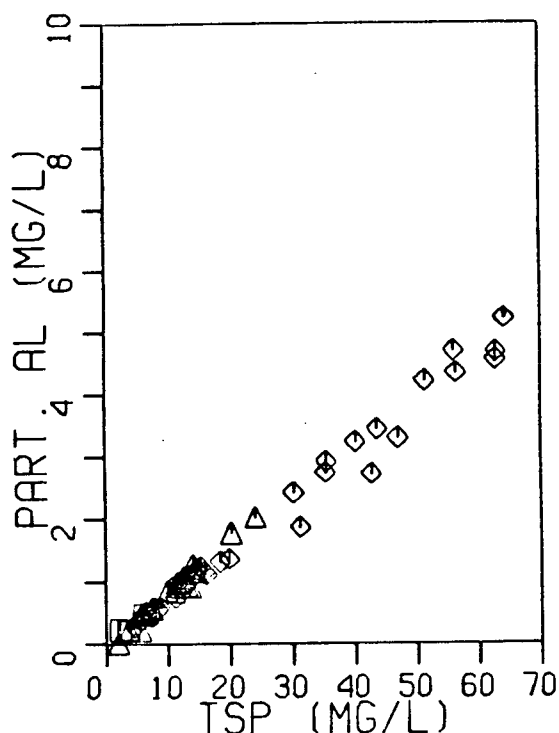


Figure 19a Cruise 78-16

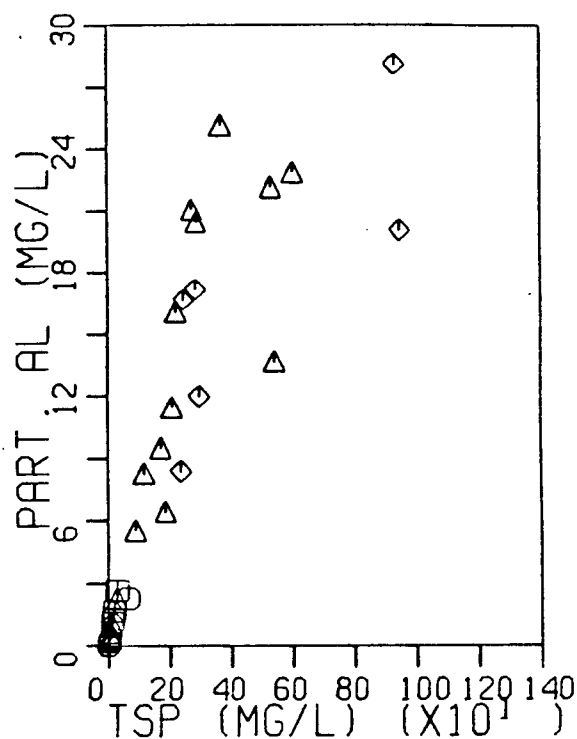


Figure 19b Cruise 79-12

FIGURE 19 Particulate aluminium concentrations plotted versus total suspended particulate concentrations for Cruises 78-16 and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Straits of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

measured in May. Regardless of the time of year, the concentration of riverine suspended particulate material exhibits considerable scatter reflecting variations in the hydrodynamics of the river flow. Pretious (1972) reported that tidal effects on the suspended load were observed as far upstream as the Port Mann Bridge (Figure 2) where ebb-tidal discharges were greater than flood-tidal discharges. Downstream variations occur due to stronger tidal effects and deposition as the river trifurcates and widens at New Westminster. Since fresh water persists at the surface as far downstream as Steveston in October and to Sand Heads in May, riverine data

exhibit considerable scatter.

Suspended particulate concentrations in the surface waters in October 1978 (Cruise 78-16, Figure 18a) decrease linearly with salinity suggesting that the suspended material behaves conservatively. Particulate aluminium data indicate similar behaviour during Cruises 78-04 and 79-01. In May 1979 (Cruise 79-12), the concentration of particulate material decreases rapidly with salinity in the initial mixing zone but, at salinities greater than 10 ppt, apparently behaves conservatively.

Bottom samples in the Fraser Estuary exhibited high concentrations of suspended material throughout the year due to resuspension of bottom sediments. The highest concentrations of suspended sediment measured at Anchor Station 56.3 during Cruise 78-16 coincided with low water slack and mid-flood (Appendix B.3). This time series of observations on waters from the salt wedge indicated that during an ebbing tide the high salinity bottom water (26.969 ppt) had a total suspended particulate concentration of only 8.33 mg/l. By contrast, at low water slack the salinity ranged from 8 to 12 ppt with suspended sediment loads of 30 to 63 mg/l. The amount of suspended material decreased somewhat as the tide started to flood but then increased to the range of 51 to 64 mg/l in high salinity samples (26.095 to 26.922 ppt) collected at approximately mid-flood. During an ebbing tide on the following day, the suspended load was only 5.60 mg/l at a salinity of 26.530 ppt. Milliman (1980) observed maximum sediment concentrations in near-bottom waters at Steveston during flood tide at times of

the year other than during the freshet.

4.4.2 The Dissolved Manganese Maximum at Low Salinity

The most striking feature observed in all the dissolved manganese plots (Figure 15) is the maximum concentration in the initial mixing zone of the estuary. The salinity of the water at this peak value varies from 4 to 12 ppt depending upon the time of sampling but from the available data appear to be independent of the daily average discharge rate of the river (Table VI). As might be expected, the maximum manganese concentration varies with the dissolved manganese concentration in the river water.

Both the establishment of the maximum dissolved manganese concentration and the salinity at which this occurs agree with case studies conducted in several other estuaries. Peak dissolved manganese concentrations were exhibited at a salinity of approximately 3 ppt in the Beaulieu Estuary (Holliday and Liss, 1976) and at 5 ppt on two occasions in both the Rhine and Scheldt Estuaries (Duinker et al., 1979b). Evans et al. (1977) observed the manganese maximum at salinities ranging from 6 to 16 ppt at three different times in the Newport Estuary. Thus, the Fraser Estuary is similar to the Newport Estuary in exhibiting temporal variations in the salinity of the manganese peak. Also, the dissolved manganese concentrations are comparable in these two estuaries. The maximum manganese concentrations observed in the Fraser and Newport Estuaries are approximately 25 ppb but exceed 100 ppb in the other case studies mentioned above.

TABLE VI Salinity and Concentration of the Dissolved Manganese Maxima

Cruise Number	Discharge Rate (m ³ /sec)	River Mean Dis. Mn (ppb)	Maximum Dis. Mn (ppb)	Salinity of Mn Maximum (ppt)
78-04	951	11.2	17.6	4.028
78-16	1900	6.61	7	4 - 8
79-01	816	15.1	23.9	8.804
79-12	7140	9.24	14.4	12.280

The source of this excess dissolved manganese remains controversial. Although data are unavailable for the anthropogenic input of manganese into the main arm of the Fraser River, some analyses of the effluent discharged from the Iona Island sewage treatment plant (Figure 5) have been reported. Since this sewage plant treats domestic sewage, industrial effluent, and storm water runoff, these data should be representative of the anthropogenic discharge into the Fraser River. Higgs (1977) reported dissolved manganese concentrations of 0.03 to 0.06 mg/l and total manganese content ranging from 0.04 to 0.08 mg/l. These concentrations are somewhat higher than riverine levels; however, the daily average discharge rates, varying from 1.67 to 12.9 m³/s during 1971/72 (Tanner et al., 1973), are insignificant in comparison to the flow rate of the Fraser River (Figure 3). Consequently, an anthropogenic origin of the excess manganese is considered to be improbable.

But, as outlined in Chapter 1, two natural sources exist. Firstly, the manganese may be released from suspended particulate material by desorption, dissolution or biological processes. Secondly, the metal may be released from estuarine bottom sediments.

4.4.3 The Role of Suspended Particulate Manganese in Establishing the Dissolved Manganese Peak

To determine the importance of the suspended particulate material in developing the dissolved manganese maximum, a number of points will be examined:

- (1) mixing experiments
- (2) comparison of the mean concentration of riverborne suspended particulate manganese with "excess" dissolved manganese
- (3) variations in the suspended particulate Mn:Al ratios versus salinity
- (4) total manganese concentration in the estuary.

Experiments were performed by mixing aliquots of river water with sea waters of varying salinities. Enhancement of dissolved manganese concentrations in the mixture, with respect to river and sea water concentrations, would indicate a particulate/dissolved interaction. Surface (fresh) and bottom (saline) samples were collected at three stations in the Fraser River with the double NIO water bottle sampler. The complete contents of one NIO bottle from each of the surface and bottom samples were mixed. The mixtures and remaining surface and bottom samples were filtered immediately and processed as

described in Chapter 2.

Results presented in Table VII indicate that within the precision of the technique, dissolved manganese concentrations in the mixture agreed with those anticipated from simply mixing river and sea waters. Thus, no desorption nor dissolution of riverborne particulate manganese was observed. This agrees with the results of similar experiments of Sholkovitz (1979) and Duinker et al. (1979b).

One of the mixtures was refiltered through a Millipore VCWP filter with a nominal pore size of 100 nm. Since the dissolved manganese concentration agreed within the precision of the technique with the mixture filtered through a Gelman Metrical GA-6 Membrane filter (nominal pore size of 450 nm), this indicates that colloids in the size range of 100 to 450 nm contribute no measurable manganese to the dissolved concentration. While a single analysis is not meant to be definitive, the result does agree with Kremling and Petersen (1978) who reported that manganese passing through a Nuclepore filter (nominal pore size of 400 nm) was present in true solution. Similarly Moore et al. (1979) found that 98 to 102% and 95 to 100 % of the dissolved manganese in River Beaulieu waters passed through filters with a nominal molecular weight cut-off of 3×10^4 and 10^5 respectively.

A second experiment was performed to examine possible release of manganese from particulate material. The dissolved manganese concentration was monitored after introducing 25.7g of riverine sediment, collected from Fort Langley, into 800ml of estuarine water (salinity = 10 ppt, pH = 7.75, temperature =

TABLE VII Mixing Experiments

Sample	Salinity (ppt)	Dis. Mn (ppb)
1 Surface	1.324	12.6
1 Bottom	27.427	8.43
1 Mixture	14.376	10.7
1 Ideal		10.5
2 Surface	0.107	8.67
2 Bottom	9.458	12.7
2 Mixture	4.783	10.7
2 Ideal		10.7
3 Surface	0.0	9.25
3 Bottom	1.0	9.00
3 Mixture	0.5	9.13
3 Ideal		9.13
3 Refiltered (100 nm)		9.29

10°C). The sediment was not dried prior to the experiment; however, the weight was measured after oven drying at 110 °C for three hours. The dissolved manganese concentration rose to 60 ppb after 4 hours and then fell to 40 ppb after 20 hours. Although these concentrations are considerably higher than those observed in the estuary, the manganese released from the sediment was only 1.7 ppm on a dry weight basis. Although it

TABLE VIII Comparison of the Mean Riverborne Suspended Particulate Manganese with "Excess" Dissolved Manganese in the Fraser Estuary

Cruise Number	Mean Particulate Manganese (ppb)	"Excess" Dissolved Manganese (ppb)
78-04	9.13	8
78-16	14.3	3.5
79-01	9.24	12
79-12	222	12

may not be possible to scale the results to suspended sediment concentrations observed in the estuary (10 to 24 mg/l in October 1978), it is evident that the riverborne suspended particulate material could not release sufficient metal to account for the observed manganese maxima.

Field data from four estuarine cruises were examined to evaluate riverborne suspended particulate material as a potential source of dissolved manganese. Table VIII compares the mean particulate manganese concentration in the Fraser River with "excess" dissolved manganese, where "excess" dissolved manganese refers to the difference between the observed amount and that which would occur as a result of conservative mixing of the two end members.

Total dissolution of the riverborne suspended particulate manganese during Cruise 79-01 could not account for the observed dissolved manganese excess. During Cruise 78-04 the mass balance could be achieved only with near-complete dissolution of

the manganese in the suspended material. This would seem to be unlikely since the suspended particulate fraction includes not only manganese bound to organic material and amorphous oxides but also residual manganese. Data from Cruises 78-16 and 79-12 indicate that riverborne suspended particulates could supply sufficient manganese to develop the observed dissolved maxima.

An alternative method of examining the field data involves plotting the ratio of the suspended particulate manganese concentration to the suspended particulate aluminium concentration versus salinity, (Sholkovitz, 1979). This normalizes the data to aluminium, an unreactive constituent in the terrigenous material which constitutes the bulk of suspended material in the Fraser Estuary. While this ratio can be influenced by variations in the grain size distribution of the suspended particulate material, the total suspended material behaves conservatively in the Fraser Estuary during non-freshet months, and therefore, the release of manganese in the initial mixing zone would be reflected in a drastic decrease of the Mn:Al ratio.

Suspended particulate Mn:Al ratios, plotted versus salinity, for Cruises 78-04, 78-11, 78-16, 79-01, and 79-12 are shown in Figure 20a through Figure 20e, respectively. Samples with suspended particulate aluminium concentrations less than 100 ppb were rejected. The suspended particulate Mn:Al ratios displayed no discernible decrease at salinities corresponding to the dissolved manganese peak. The Mn:Al ratios for Cruises 78-04, 78-11, and 79-01 are very similar, falling in the range 10 to 12×10^{-3} . Data from Cruise 78-16 show more scatter and

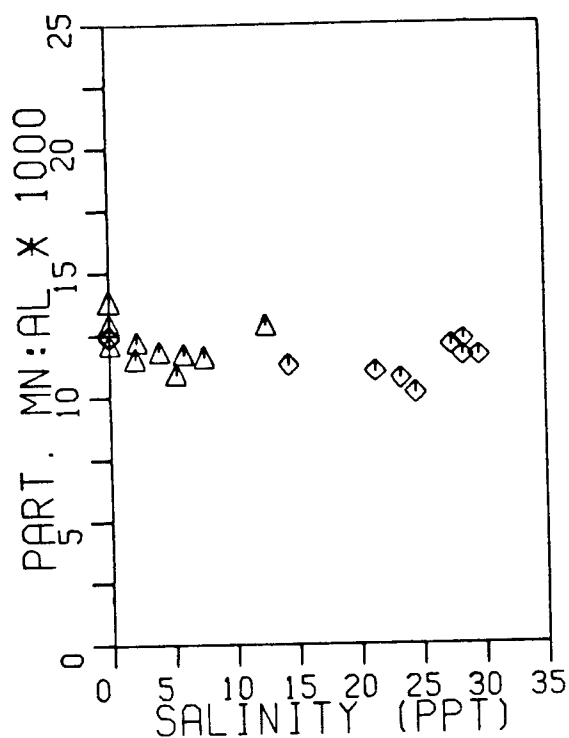


Figure 20a Cruise 78-04

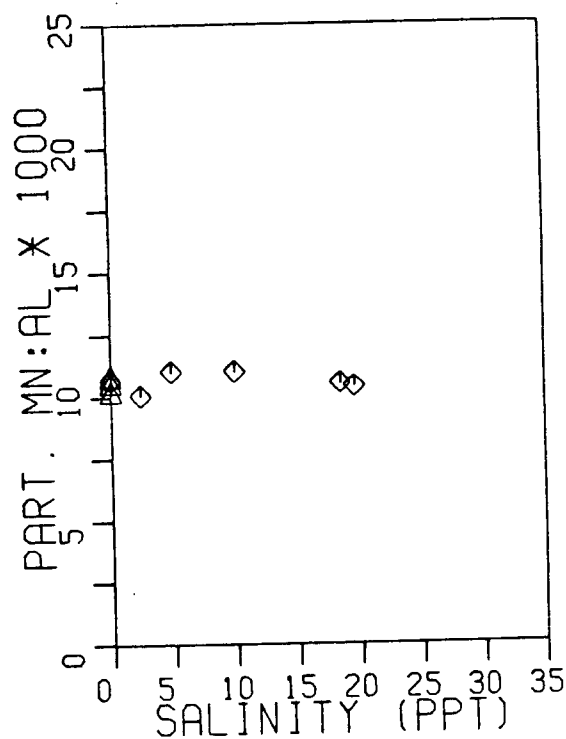


Figure 20b Cruise 78-11

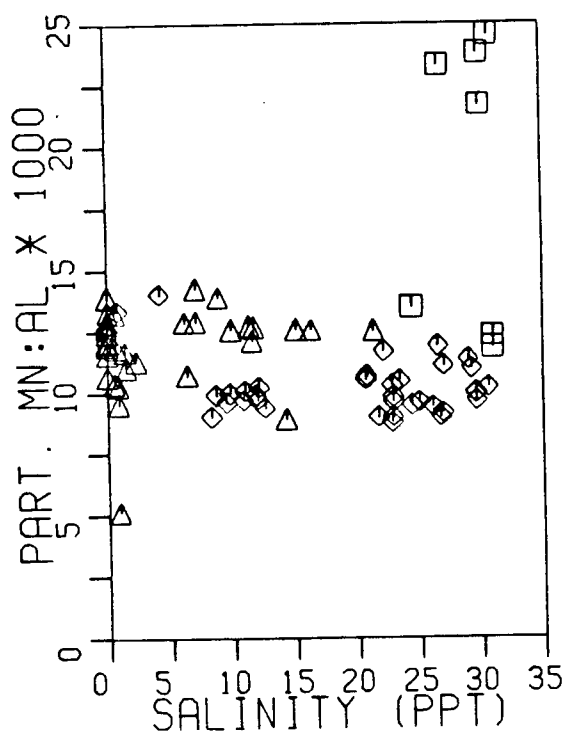


Figure 20c Cruise 78-16

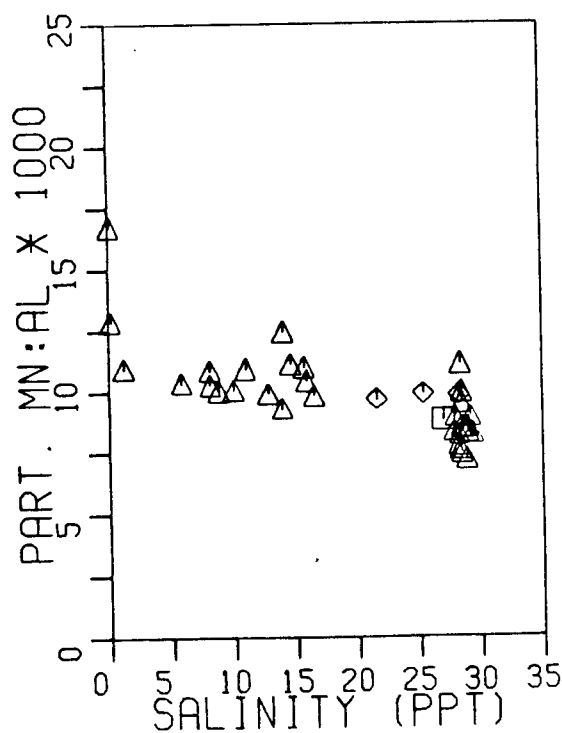


Figure 20d Cruise 79-01

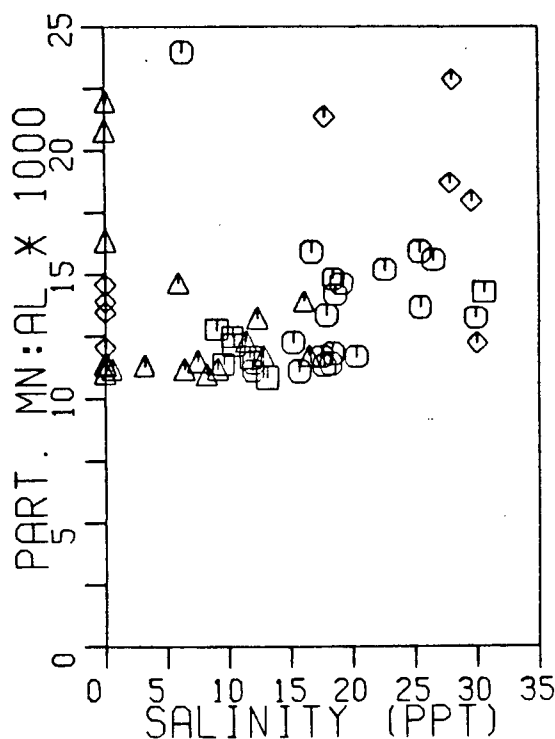


Figure 20e Cruise 79-12

FIGURE 20 Particulate Mn:Al ratios plotted versus salinity for Cruises 78-04, 78-11, 78-16, 79-01, and 79-12. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

Mn:Al ratios in the salt wedge were lower than those in surface waters of comparable salinity. This indicates compositional differences between the riverborne suspended particulate material and the resuspended sediment. This will be discussed further in the following section. Data for Cruise 79-12 (Figure 20e) differ somewhat from data at other times. The aluminium content of the suspended particulate material varies considerably at this time (Figure 19), and therefore, Mn:Al ratios exhibit scatter due to variations in grain size effects. This is particularly evident in the riverine samples. The suspended particulate Mn:Al ratio tends to increase as the salinity increases, but higher salinity samples occur in the

Strait of Georgia. Suspended particulate Mn:Al ratios in the salt wedge are also quite high. Despite these differences, the ratios in surface waters in the mixing zone are similar to those observed at other times of the year, even though the absolute concentrations are orders of magnitude greater than measured during periods of lower discharge.

Finally, if the dissolved manganese maximum resulted from an interaction between the dissolved and particulate components, the total manganese should behave conservatively. As indicated in plots of total manganese versus salinity (Figure 21a through Figure 21c), conservative behaviour was not evident in the surface waters for Cruises 78-04 and 79-01. At both these times the maximum dissolved concentration corresponded to the maximum total concentration. The significance of the results from Cruise 78-16 (Figure 21b) is somewhat less certain; however, the data would seem to suggest that the total manganese concentration in samples from the initial mixing zone lie above the conservative mixing curve. Data for Cruise 79-12 was not plotted due to the overwhelming contribution of the particulate fraction to the total manganese during the freshet.

Riverborne suspended material possibly acts as a source of dissolved manganese during the freshet when suspended levels are exceptionally high. The surface samples from Station 53 (Cruise 79-12), with anomalously high dissolved manganese concentrations, were associated with high suspended sediment loads. Milliman (1980) observed similarly high suspended sediment levels, greater than 400 mg/l, in surface offshore waters during the freshet which he attributed to the

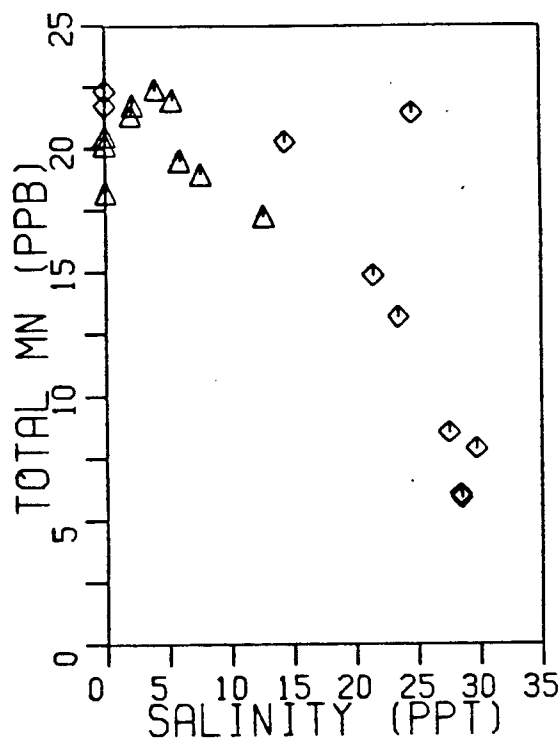


Figure 21a Cruise 78-04

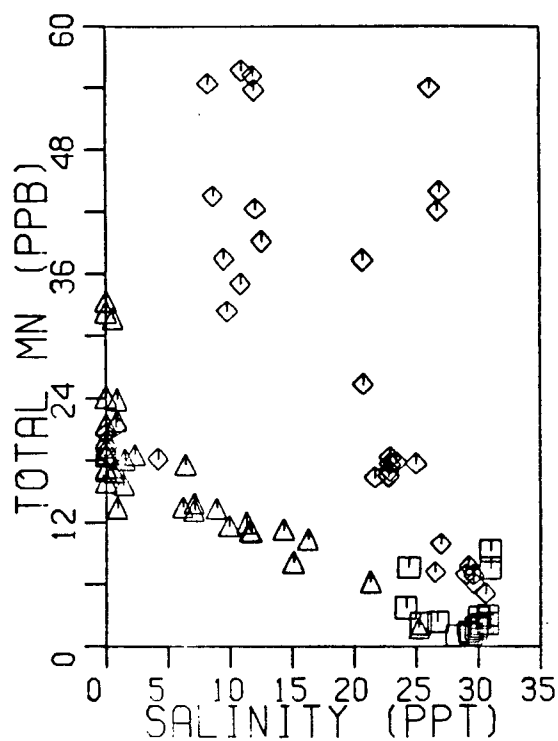


Figure 21b Cruise 78-16

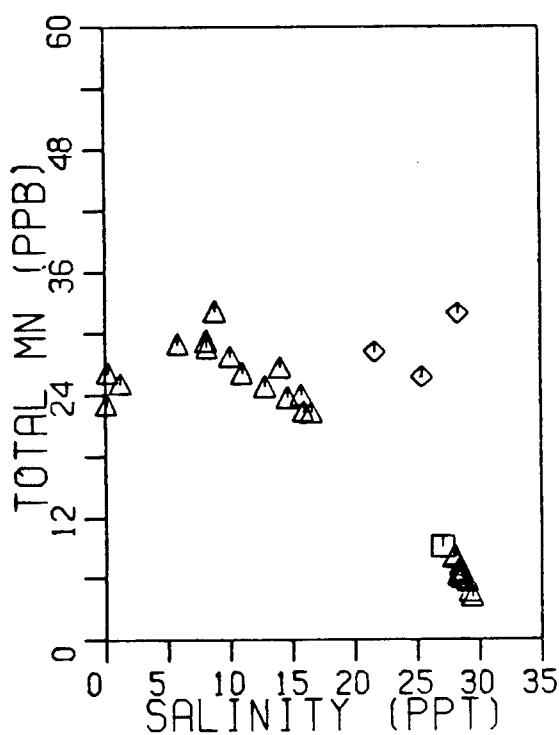


Figure 21c Cruise 79-01

FIGURE 21 Total manganese data plotted versus salinity for Cruises 78-04, 78-16, and 79-01. Symbols: \square data at all depths for Station 15; \circ data at all depths at other stations in the Strait of Georgia; \triangle surface samples in the Fraser Estuary; \diamond bottom samples in the Fraser Estuary.

resuspension of bottom sediments.

The dissolution or desorption of manganese from riverborne suspended particulate material would not be likely to account for the manganese enrichment observed at other times of the year. Experimental evidence indicates that dissolved manganese concentrations in mixtures of fresh and saline waters agree with results anticipated from physical mixing processes alone. Riverine sediment suspended in estuarine water released only 1.7 ppm manganese on a dry weight basis, insufficient to account for the dissolved manganese peak in the Fraser Estuary as suspended sediment loads often fall in the range of 10 to 24 mg/l. A geochemical mass balance between riverborne suspended particulate manganese and estuarine "excess" dissolved manganese cannot be attained at some times of the year, even with complete dissolution of all the suspended particulate manganese. The suspended particulate Mn:Al ratio does not change significantly in the estuary. Finally, the concentration of total manganese exhibits a maximum at low salinity on at least two occasions.

For these reasons, the estuarine bottom sediments must supply overlying waters with dissolved manganese. Evans et al. (1977) proposed that manganese was remobilized from sediments following the reduction of manganese oxides. Should this be the case in the Fraser Estuary, one would anticipate elevated dissolved manganese concentrations in both the salt wedge and interstitial waters of the sediments.

4.4.4 The Role of Estuarine Bottom Sediments in Establishing the Dissolved Manganese Peak

In examining the estuarine sediments as a potential source of the dissolved manganese maximum in the surface waters, five aspects to be considered are:

- (1) dissolved manganese concentrations in salt wedge waters
- (2) dissolved manganese concentrations in the interstitial waters of estuarine sediments
- (3) ammonium oxalate extractable manganese in estuarine sediments
- (4) variations in the Mn:Al ratios in estuarine sediments
- (5) mass balance calculations for manganese

Most studies of the manganese distribution in estuarine waters have focussed on the surface waters. Graham et al. (1976) reported enhanced concentrations in bottom waters compared to surface waters in Narragansett Bay; however, these few samples were restricted to salinities greater than 27 ppt. Bottom waters in the Fraser Estuary were collected to determine the manganese distribution through the complete salinity range at various times of the year.

Elevated dissolved manganese concentrations were observed in the salt wedge on several occasions suggesting that the sediments do indeed act as the source of extraneous manganese (Figure 15). Although the dissolved manganese concentration in Fraser River water during Cruise 78-11 (Appendix B.1) ranged from only 1.97 to 2.93 ppb, five bottom water samples collected

near Steveston exhibited concentrations as high as 13.3 ppb at a salinity of 19.580 ppt. The manganese content increased with salinity in these bottom samples, possibly because the samples were obtained on a flooding tide shortly after the toe of the salt wedge passed the collection site.

The few salt wedge samples obtained during Cruise 79-12 (Figure 15d) exhibited dissolved manganese concentrations higher than observed in surface waters of comparable salinity. This was particularly evident for bottom waters with a salinity greater than 25 ppt.

Similarly, during Cruise 78-16 (Figure 15b) estuarine bottom waters exhibited dissolved manganese concentrations higher than observed in surface waters of comparable salinity, especially at salinities greater than 20 ppt. While concentrations in the surface waters of the Fraser River were as high as 18.8 ppb in the previous week, peak manganese concentrations near 7 ppb were observed during the cruise at salinities ranging from 2.282 to 14.295 ppt. In comparison, bottom waters in this salinity range exhibited concentrations between 8 and 10 ppb.

Included among the salt wedge data from Cruise 78-16 is a partial time series at Station 56.3 (Appendix B.3). The dissolved and suspended particulate manganese data, plotted versus salinity, from this station are presented in Figures 22a and 22b respectively. Numbers used to identify water samples in the following discussion refer to these figures.

On an ebbing tide, the bottom water (1) had a salinity of 26.969 ppt and a dissolved manganese concentration of 3.62 ppb.

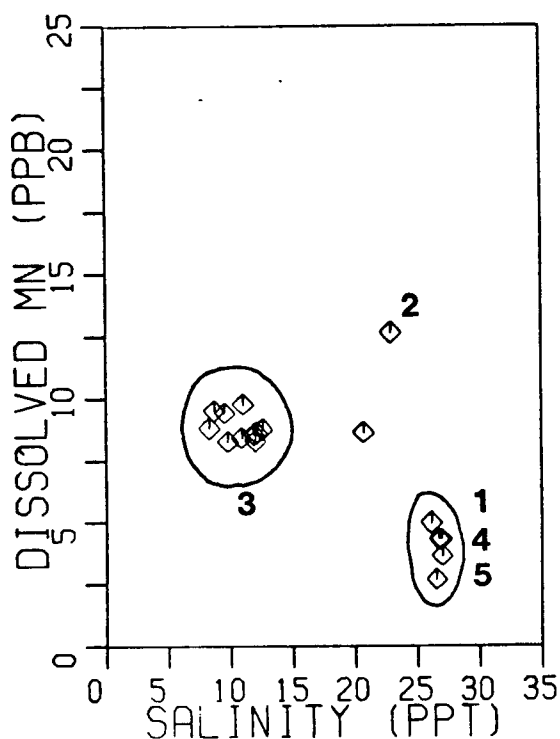


Figure 22a Dissolved Mn

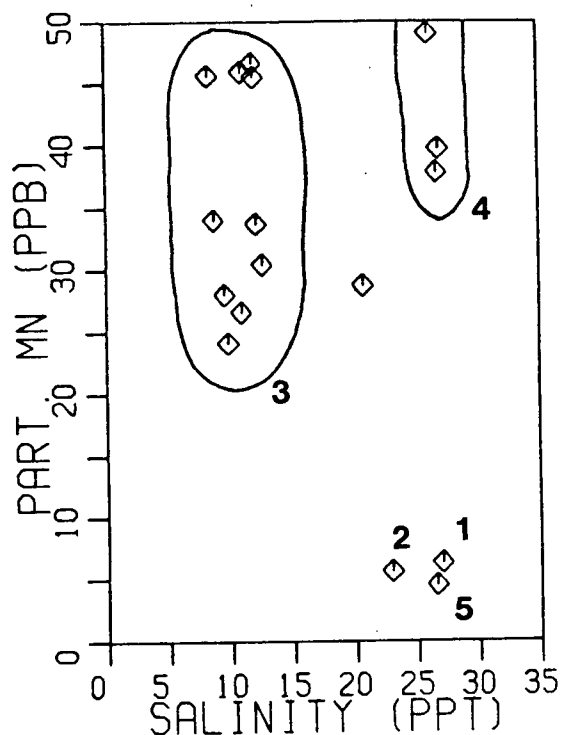


Figure 22b Particulate Mn

FIGURE 22 Dissolved and Particulate Manganese concentrations, plotted versus salinity, for bottom waters from Station 56.3, Cruise 78-16 only.

The suspended particulate manganese content was 6.30 ppb. A sample (2) with a salinity of 22.925 ppt had an anomalously high dissolved manganese content (12.6 ppb) and a low suspended particulate manganese content (5.60 ppb). Samples collected from the toe of the salt wedge during low water slack (3) had salinities ranging from 8 to 12 ppt with dissolved and suspended particulate manganese concentrations of 8 to 10 ppb and 25 to 47 ppb, respectively. As the tide flooded (4), the salinity and dissolved manganese returned to former levels, 26 ppt and 3 ppb, respectively. Suspended particulate manganese concentrations initially remained high, 38 to 49 ppb. However, during an ebbing tide on the following day (5), the concentration had decreased to 4.5 ppb. While one sample (2) behaves anomalously,

these data indicate that the elevated dissolved manganese concentrations in estuarine bottom waters are generally associated with sediments resuspended due to tidal scouring upriver from Steveston. This was also observed during Cruise 78-11, as discussed previously.

Thus, the field data indicate that significant dissolved manganese enrichment occurs in the salt wedge throughout the year, and that the source of manganese must lie in the estuarine sediments. The metal may be released into overlying salt wedge waters by two mechanisms. Firstly, as suggested by Evans et al. (1977), reduction of manganese oxides in the sediments could concentrate dissolved manganese in the interstitial waters. Subsequent release of this interstitial water could then occur by the turbulent resuspension of the sediments. Manganese dissolved in interstitial waters could also be introduced into overlying waters via molecular diffusion or bioturbation. Secondly, the manganese may be desorbed (or dissolved) from the estuarine sediment resuspended due to tidal scouring.

Sediments from several estuaries have been reported to exhibit elevated dissolved manganese concentrations in interstitial waters (Evans et al., 1977; Sanders, 1978a; Eaton, 1979; and Elderfield et al., 1979). Some cores collected both in February 1979 and January 1980 from the lower reaches of the Fraser Estuary had interstitial waters considerably enriched in dissolved manganese.

While some samples analysed had dissolved manganese concentrations ranging from 19 to 126 ppb only, concentrations in the ppm range were measured in the interstitial waters of

sediments from Stations 56.2 and 59 in February 1979 (Appendix C.2) and again from Station 56.2 in January 1980 (Appendix C.5). Thus, some interstitial waters exhibit dissolved manganese levels enriched as much as three orders of magnitude over concentrations in estuarine waters. Incorporation of these interstitial waters into overlying waters would lead to considerable enrichment. At the same time, the dissolved manganese in the interstitial waters would be depleted. Thus, interstitial waters may have been removed from those cores exhibiting relatively low concentrations of dissolved manganese (less than 150 ppb).

The volume of interstitial water required to account for the dissolved manganese enrichment in the surface waters can be estimated by assuming the dissolved manganese concentration in the interstitial waters is approximately 10 mg/l and a dilution factor of $1:10^3$ with Fraser River water. Since the Fraser River discharge, measured at Mission (Figure 2), is approximately 90.0×10^{12} l/yr (Water Survey of Canada, 1978 and 1979), 90.0×10^9 l/yr of interstitial water would be necessary. Assuming that the area of the river channel affected by the salt wedge is approximately 15 km by 300 m (4.5×10^{10} cm²), the net exchange of interstitial water would be 2.0 l/cm²/yr or 5.5 ml/cm²/day. This would correspond to a dissolved manganese efflux of 55 μ g/cm²/day, an order of magnitude greater than diffusive fluxes reported for Narragansett Bay (Graham et al., 1976), Chesapeake Bay (Eaton, 1979) and the Rhine/Scheldt Estuaries (Duinker et al., 1979b).

The diffusive flux (F) of dissolved manganese from Fraser

Estuary sediments, a lower limit for the rate of supply of manganese, can be estimated using Fick's first law:

$$F = -(dc/dx) D$$

where D , the diffusion coefficient, is taken to be $2 \times 10^{-6} \text{ cm}^2/\text{sec}$ (Eaton, 1979). The dissolved manganese concentration in the interstitial water increases to $11 \mu\text{g}/\text{ml}$ at a depth of 7.5 cm in sediments collected at Station 56.2 in February 1979 (Appendix C.2). This gives a dissolved manganese flux of approximately $0.3 \mu\text{g}/\text{cm}^2/\text{day}$. The discrepancy between this value and the previously calculated flux indicates that molecular diffusion of manganese from interstitial waters into the overlying salt wedge cannot be solely responsible for the dissolved manganese enrichment in the surface waters of the Fraser Estuary.

Accordingly, the desorption or dissolution of manganese from resuspended estuarine bottom sediments must contribute significantly to the observed manganese enrichment. Manganese release from the resuspended material may occur in response to the increase in ionic strength or, alternatively, due to the slight decrease in the pH of the bottom water as the salt wedge advances. The high dissolved manganese concentrations observed in surface waters at Station 53 during Cruise 79-12 were also associated with resuspended bottom sediments (see Section 4.4.3).

Results from the analyses of the estuarine bottom sediments suggest that the removal of manganese from these sediments may occur. It should be noted that the surficial sediments are transported through the Fraser Estuary as bedload material

rather than being deposited. Moreover, because the grain size varies little down the estuary (Appendix C.6), it should be possible to compare sediments from different sites in terms of their content of ammonium oxalate extractable manganese and Mn:Al ratio.

The concentration of ammonium oxalate extractable manganese in surface sediments decreases systematically down the estuary. This trend was observed both in May 1979 (Appendix C.3) and January 1980 (Appendix C.5). Leachable manganese concentrations in riverine sediments collected from New Westminster were 125 to 130 ppm in May 1979 and 161 to 168 ppm in January 1980. At Steveston (Station 56.2) these levels had dropped to 102 and 80.2 ppm, respectively. Sediments collected downstream of Steveston in May 1979 were further depleted in manganese, having concentrations of approximately 73 ppm. A greater concentration of extractable manganese, 153 ppm, was found at Station 53, possibly associated with the higher content of fine-grained material.

Pharo (1972) also reported differences in the content of ammonium oxalate extractable manganese in Fraser River sediments relative to sediments collected near Sand Heads. Concentrations in these sediments ranged from 176 to 226 ppm and from 88.0 to 91.2 ppm, respectively. The absolute concentrations may be higher due to his longer extraction time, 4 hours compared to 2 hours in this study.

While the amount of ammonium oxalate extractable manganese in surficial sediments collected in May 1979 decreases downstream from Steveston (with the exception of Station 53),

ammonium oxalate extractable manganese concentrations are higher in sediments from Stations 54 and 55 than observed in sediments from upstream locations (Appendix C.3). These variations are not related to the mean grain size of the sediments (Appendix C.6). Downstream variations in the metal content of bottom sediments in the Rhine and Elbe Estuaries has been attributed to physical mixing of riverine and marine sediments (Müller and Förstner, 1975). However, this process does not occur in the Fraser Estuary during the freshet because the near-bottom transport of sediments is seaward only (Milliman, 1980). Alternatively, the increase in the ammonium oxalate extractable manganese may be related to variations in the mineralogical composition of the sediments in the lower reaches of the estuary. Such mineralogical variations may also account for the difference between the ammonium oxalate resistant aluminium and the total aluminium concentrations (Appendix C.3). The ammonium oxalate resistant aluminium constituted 89 to 98% and 62 to 78% of the total aluminium content in sediments collected upstream and downstream, respectively, from Station 55.

The Mn:Al ratios in the sediments are lower than observed in riverborne particulate material. Sediments collected during Cruise 79-12 from stations throughout the Fraser Estuary display ratios ranging from 5.89 to 9.77×10^{-3} (Table IX). Mn:Al ratios in suspended particulate material sampled at this time always exceeded 10.0×10^{-3} (Figure 20e). Since the bottom (bedload) and suspended sediments in the Fraser Estuary share a common source, the differences in the Mn:Al ratios may be due to either variations in the ratio as a function of the grain size

TABLE IX The Mn:Al Ratio in Surficial Estuarine Sediments
Collected in May 1979 (Cruise 79-12)

Station Number	Mn:Al Ratio ($\times 10^3$)
3	17.7
15	4.57
53	5.89
54	7.12
55	9.77
56	7.85
59	7.36
65	8.14

or the result of diagenetic processes in the sediments.

As previously mentioned, Mn:Al ratios for sediments obtained in January 1980 will tend to exceed the true values due to loss of aluminium during the ammonium oxalate extraction. However, these values (8.85 to 10.2×10^{-3}) again are lower than the Mn:Al ratios generally observed in estuarine particulate material (Figure 20c). It should be noted that low ratios found in the particulate material in the salt wedge during Cruise 78-16 (Figure 20c) may be explained by resuspension of these bottom sediments.

A mass balance for manganese was calculated to test the hypothesis that the estuarine sediments could supply sufficient dissolved manganese to maintain the observed maximum in surface waters. The Fraser River discharge, measured at Mission (Figure 2), is approximately 90.0×10^{12} l/yr (Water Survey of Canada, 1978 and 1979). Assuming the excess dissolved manganese in the river water is approximately $10 \mu\text{g/l}$ (Table VIII), the efflux of

excess manganese would be 9.0×10^5 kg/yr. The concentration of oxalate extractable manganese in surficial sediments decreases by approximately 65 ppm (Appendices C.3 and C.5) as these sediments are transported from New Westminster to Steveston. Assuming that this decrease results from chemical rather than physical processes in the estuary, an annual bedload of 1.4×10^{10} kg would be required to balance the observed manganese enhancement. Although there are no measurements of bedload transport through the Fraser Estuary for 1978 or 1979, Pretious (1972) estimated the potential bedload passing New Westminster to be 16.2×10^6 tons/yr or 1.5×10^{10} kg/yr. The agreement between these values suggests that the bottom sediments could act as a source of manganese.

Summarizing, the field data suggest that the excess dissolved manganese observed in the surface waters may be derived from estuarine bottom sediments. Throughout the year the concentration of dissolved manganese in the salt wedge exceeds levels in surface waters of comparable salinity. Enhanced manganese content in the bottom waters appears to be coupled to the tidal resuspension of sediments in the Fraser Estuary. This dissolved manganese enrichment may occur due to desorption (or dissolution) from the resuspended bottom sediments together with the concurrent release of some interstitial water having high concentrations of dissolved manganese due to in situ reduction of amorphous manganese oxides. The occurrence of such processes is further suggested by a general downstream decrease in the ammonium oxalate extractable manganese content in estuarine surficial sediments,

together with Mn:Al ratios in these sediments lower than observed in riverborne suspended particulates. Finally, the calculated bedload required to achieve mass balance of manganese in the system agrees with estimates of bedload transport in the Fraser Estuary (Pretious, 1972).

While the data indicate that the salt wedge waters are enriched with manganese, this bottom water must be introduced into the overlying water in a manner which satisfies the observed surface distribution of dissolved manganese throughout the Fraser Estuary. Such a mechanism will be discussed in a subsequent Section.

4.4.5 Dissolved Manganese Removal Processes

Two mechanisms may lead to the transfer of manganese from the dissolved to the particulate component in the estuarine environment. The precipitation of manganese dioxide should occur due to thermodynamic considerations (Duinker et al., 1979b). Alternatively, association with iron hydroxide and/or humate flocculation processes has been shown to cause the removal of manganese from solution in mixing experiments (Sholkovitz, 1976 and 1978). Regardless of the mechanism involved, this dissolved/particulate interaction plays an important role in the manganese recycling model proposed by Evans et al. (1977).

Field studies have established variations in the estuarine chemistry of manganese. The removal of dissolved manganese has been observed in three rivers in Georgia (Windom et al., 1971), in Narragansett Bay (Graham et al., 1976) and in the Rhine and

Scheldt Estuaries (Duinker et al., 1979b). However, dissolved manganese was shown to behave conservatively in the lower reaches of the St Lawrence (Subramnian and d'Anglejan, 1976) and the Beaulieu Estuaries (Holliday and Liss, 1976; Moore et al., 1979).

The Fraser Estuary conforms to this second category. Considering the distribution of dissolved manganese, removal from solution would develop a dilution curve that lies below the theoretical mixing line for Fraser River and Strait of Georgia waters (Figure 1). Since a dissolved manganese influx at low salinity has been observed throughout the year in the Fraser Estuary, the field data consistently lie above the theoretical dilution curve for these two end members. In order to examine the dissolved manganese data, the initial end member may be redefined as the low salinity water at the manganese peak. Subsequent removal processes in the lower reaches of the estuary would be indicated by values falling below the theoretical dilution line generated by considering mixing of Strait of Georgia water with this low salinity water.

Plots of dissolved manganese versus salinity (Figure 15) suggest no evidence for manganese removal at intermediate salinities at any time of the year when examined in terms of this redefined ideal mixing curve.

Similarly, in situ production of particulate manganese would cause positive deviations from the theoretical mixing curve of particulate manganese. This holds true in the lower reaches of the Fraser Estuary for two reasons. Firstly, since the total suspended particulates behave conservatively in the

surface waters, any increase in the particulate manganese concentration indicates removal from solution. Secondly, the concentrations of dissolved and particulate manganese are of the same order of magnitude except during the freshet. However, the distribution of particulate manganese versus salinity (Figure 16) suggests that should the oxidative precipitation of manganese occur, it is insufficient to affect the bulk distributions of the dissolved and particulate manganese components in the estuary.

Any dissolved/particulate interactions would also alter the particulate Mn:Al ratios in the lower reaches of the estuary. Manganese precipitation would increase this Mn:Al ratio at higher salinities; however, the field data (Figure 20) show no evidence for such behaviour. The Mn:Al ratios for particulate material in surface waters remain fairly uniform. This was not the case during the freshet (Figure 20e); however, the increase of Mn:Al ratios with salinity at this time is probably due to sedimentological and hydrological processes rather than chemical ones. This concept will be more fully developed in the following chapter.

Recapitulating, the removal of dissolved manganese from surface waters in the lower reaches of the Fraser Estuary, either by the oxidative precipitation of manganese or coprecipitation with colloidal iron humates and/or hydrous oxides, does not appear to be a significant process. Instead, the particulate manganese behaves conservatively and the particulate Mn:Al ratios remain relatively constant throughout the estuary.

4.4.6 Manganese Behaviour: Thermodynamic and Kinetic Considerations

Wollast et al. (1979) determined the distribution of both pH and dissolved manganese in the Rhine and Scheldt Estuaries and noted that the pH minimum corresponded with the dissolved manganese maximum. They assumed that the low pH developed due to variations in the salinity dependence of the dissociation constants of carbonic acid (Mook and Koene, 1975) and suggested that the enhanced manganese concentration resulted directly from the low pH.

Accordingly, they developed a model to determine if the behaviour of manganese during mixing in an estuary could be explained in terms of simple equilibrium relationships. This model calculates the concentration of dissolved manganese which should exist in equilibrium with various solid phases (MnCO_3 , MnOOH , MnO_2), taking into account ion pairing with chloride and sulphate ions. They defined the Eh by the following relationship based on the $\text{O}_2/\text{H}_2\text{O}_2$ couple (Breck, 1972):

$$\text{Eh} = 1.012 - 0.059 \text{ pH} + 0.030 \log p\text{O}_2$$

Calculated dissolved manganese concentrations agreed with observed field data suggesting that dissolved concentrations in the Rhine and Scheldt Estuaries are controlled by changes in the equilibrium conditions. However, in these estuaries the high manganese levels (greater than 500 ppb in some cases) are associated with anoxic waters where the concentration is determined by the solubility of manganous carbonate. Hence, the dissolved manganese maximum results from the reductive dissolution of manganese oxides associated with riverborne

suspended particulate material.

Similar calculations performed with field data from the Fraser Estuary indicate that the observed dissolved manganese concentrations always exceeded calculated equilibrium values. In contrast to the polluted Rhine, the Fraser Estuary remains well-oxygenated (Figure 7) and throughout the estuary the equilibrium concentration is determined by the low solubility of manganese dioxide. Thus, the dissolved manganese peak cannot be attributed to redox processes in estuarine waters. Furthermore, the dissolved manganese maximum occurs at a slightly higher salinity than the pH minimum suggesting that these two features are not directly interrelated.

The rate of manganese oxidation depends upon both the pH and partial pressure of oxygen. Experiments cited in Stumm and Morgan (1970) indicated that only at pH values greater than 8.5 was measurable manganese oxygenation observed within hours. Such pH values are rarely encountered in the marine environment and were exhibited in the Fraser Estuary only during periods of intense photosynthetic activity (Figure 8d).

The oxidation proceeds via an autocatalytic reaction due to Mn^{2+} adsorption onto manganese dioxide surfaces. However, Wollast et al. (1979) demonstrated experimentally that biological processes may catalyze manganese dioxide precipitation in estuarine waters.

It should be noted that in estuaries for which manganese precipitation has been well substantiated, the waters have residence times significantly longer than in the Fraser Estuary. During summer months, waters in Narragansett Bay have a

residence time of approximately one month (Graham et al., 1976). The Rhine and Scheldt Estuaries have residence times on the order of a few days and two months respectively. This compares to the Fraser Estuary which is flushed of salt with each tidal cycle (Hodgins, 1974). Thus, although the Fraser Estuary is supersaturated with respect to manganese dioxide, residence times are too short to allow significant precipitation to occur. This process is probably confined to the Strait of Georgia where the residence time of the water is considerably longer.

4.5 A Model for Manganese Behaviour in the Fraser Estuary

The field data will be briefly summarized by considering a general descriptive model of the manganese chemistry and hydrodynamics of the Fraser Estuary which accounts for all the observed features in the distribution of both dissolved and particulate manganese. After dividing the field area into three environments (river, estuary and sea) and the manganese into three components (dissolved, particulate and sediments), a simple flow diagram (Figure 23) illustrates the transport of manganese through the system. Solid lines represent observed interactions and dashed lines represent processes reported in other case studies. Interactions in the "sea" have been included for completeness but will be discussed in the following chapter.

Dissolved manganese passes through the Fraser Estuary with no perceptible oxidative precipitation nor coprecipitation with flocculated colloidal iron oxyhydroxides. The maximum concentration at low salinity arises due to the release of

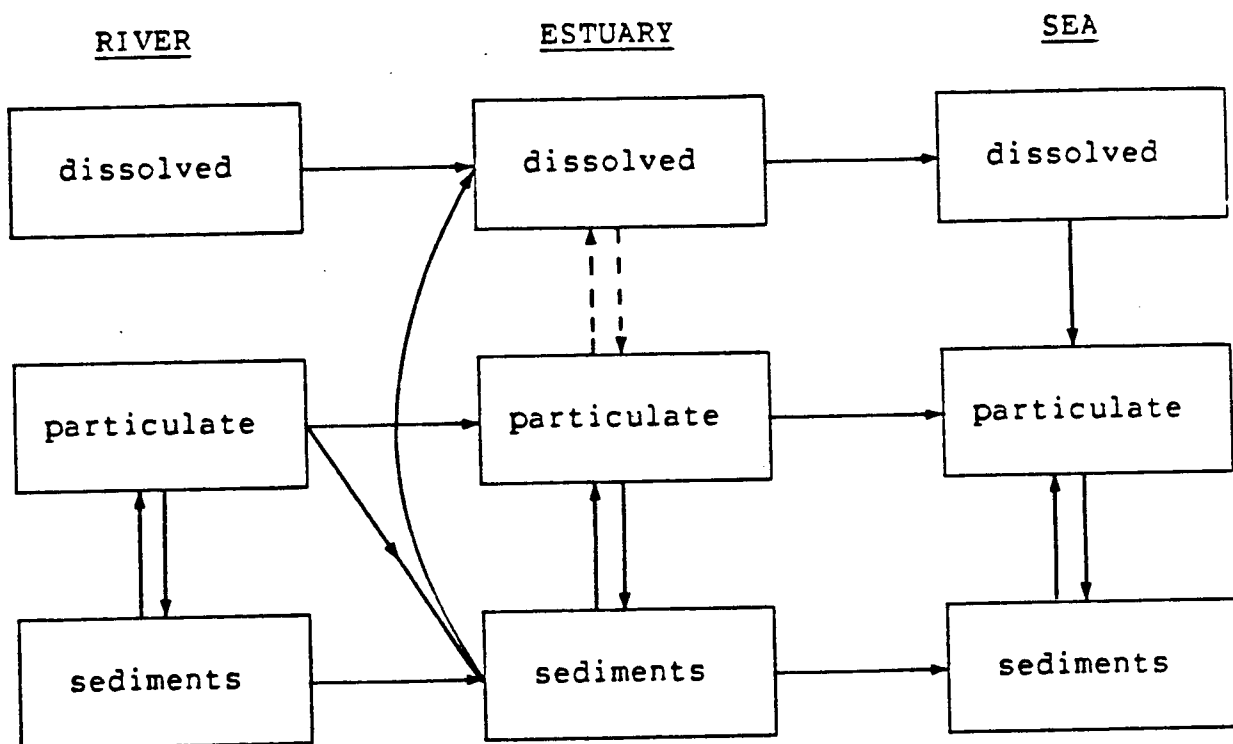


FIGURE 23 Flow diagram for the transport of manganese through the Fraser Estuary. Solid lines represent observed interactions while dashed lines represent processes reported in other estuaries.

manganese from the bottom sediments rather than from riverborne suspended particulate material.

Following the deposition of some particulate manganese in the river and upper reaches of the estuary due to changes in the hydrodynamics of the river, the particulate manganese generally behaves conservatively. Tidal resuspension of estuarine sediments causes enhanced concentrations of particulate manganese in salt wedge waters during ebb-tidal flows. Most of this material seems to be redeposited as the discharge rate decreases with a flooding tide.

Both in the river and estuary, surficial sediments comprise the bed load and as such can be considered to be transported

through the system. Diagenetic processes in the estuarine bottom sediments concentrate manganese in the interstitial waters of these sediments. Tidal resuspension of the sediments releases these waters into the salt wedge. The concurrent desorption or dissolution of manganese from these resuspended sediments causes the enrichment of dissolved manganese observed in water of the salt wedge.

Thus, the available evidence indicates that the dissolved manganese maximum in the surface waters results from the mixing of Fraser River water with manganese-enriched water from the salt wedge. This bottom water must be introduced into overlying water in a manner which satisfies the observed surface distribution of dissolved manganese throughout the Fraser Estuary. This distribution can be considered to consist of two conservative dilution curves which intersect at the salinity and manganese concentration corresponding to the dissolved manganese maximum.

Data from Cruise 78-16 (Figure 15b) indicate that in the bottom waters, the highest dissolved manganese concentrations occur in the toe of the salt wedge. Vertical advection of these waters and subsequent entrainment into the outflowing river discharge causes an increase in the dissolved manganese concentration in the surface waters concurrently with an increase in salinity. The mixing of manganese-enriched water from the salt wedge with river water corresponds with the conservative dilution curve observed at low salinities. Furthermore, this mixing process forms a discrete water mass at the surface with salinity and dissolved manganese concentrations

corresponding to those of the manganese peak. Considering the case during Cruise 78-16 (Figure 15b), conservative mixing of Fraser River water with bottom waters could lead to the development of an "Intermediate" Water mass having a salinity of 5 to 6 ppt and a dissolved manganese concentration between 6 and 9 ppb. Subsequent dilution of this Intermediate Water with sea water from the Strait of Georgia (with dissolved manganese concentrations in the order of 1 to 4 ppb) establishes the conservative mixing curve observed at higher salinities.

These processes can be illustrated with a schematic diagram of the longitudinal distribution of salinity and dissolved manganese from Cruise 78-04 (Figure 24). Inflowing saline water becomes enriched with the dissolved manganese released with the resuspension of sediments. Maximum enrichment occurs in the toe of the salt wedge. Entrainment of these waters and mixing with the outflowing river water causes a downstream increase in the dissolved manganese concentration, and eventually establishes the peak at an approximate salinity of 4 ppt. Subsequent mixing involves saline waters with relatively low manganese concentrations and, therefore, surface concentrations decrease. Although bottom samples from the toe of the wedge were not obtained at this time, this model suggests concentrations would have been in the range of 8 to 10 ppt for the salinity and 20 to 22 ppb for the dissolved manganese.

Salt wedge water of varying salinities may be enriched in manganese depending on the state of the tide or position in the estuary. Accordingly, the different dissolved manganese maxima observed on different days may be explained either by short term

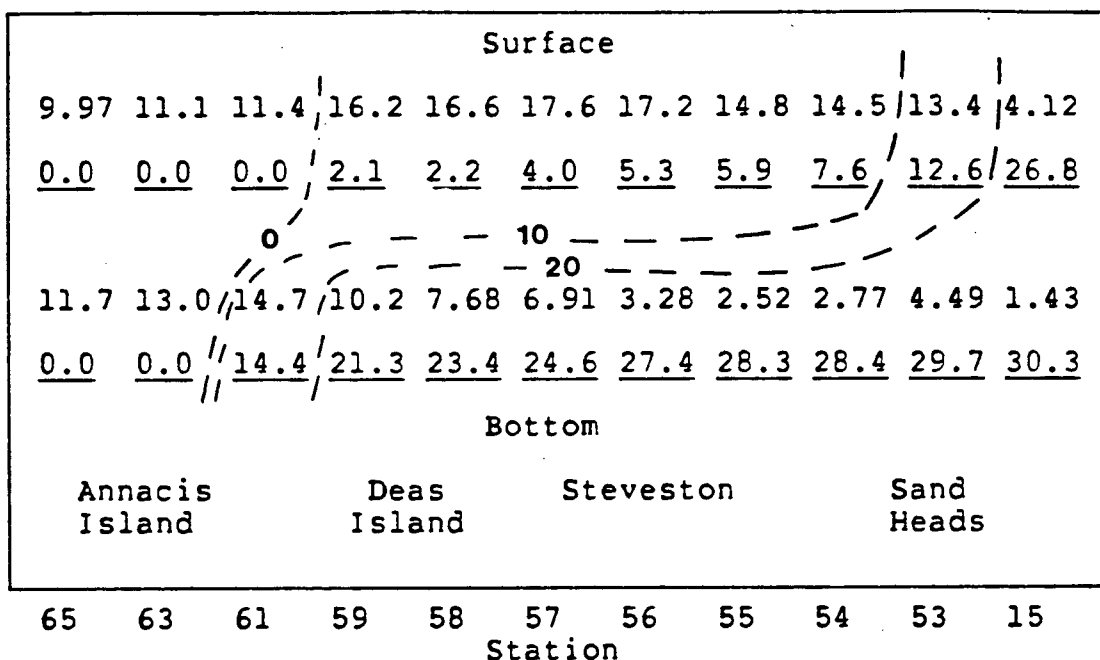


FIGURE 24 Schematic diagram of the longitudinal distribution of dissolved manganese (ppb) and salinity (ppt) from Cruise 78-04. Salinity values are underlined and contoured. The water depth at Station 15 is 177 m but varies in the range of 6 to 20 m for Stations 53 to 65.

variations in the Fraser River manganese content or by the vertical advection of salt wedge waters with comparable dissolved manganese concentrations but different salinities. Seasonal variations in the absolute concentration of the peak (Table VIII) may also be controlled by such processes.

The dissolved manganese data concur with the pH data. The distribution in surface waters for both these parameters is best explained in terms of a two step mixing process. While the manganese peak occurs at a higher salinity than the pH minimum, these features are both caused by entrainment of salt wedge water. Finally, despite the non-linear variation of dissolved manganese with respect to salinity, this metal behaves

conservatively in the surface waters of the Fraser Estuary and chemical reactivity appears to be restricted to the estuarine bottom sediments.

5. MANGANESE DISTRIBUTION IN THE STRAIT OF GEORGIA

5.1 Preamble

Cruises were conducted throughout the central and southern portions of the Strait of Georgia during January and May in both 1978 and 1979. These sampling periods preceded the dates of seasonal extremes of the Fraser River discharge by approximately one month (Table II).

The surface distribution of water parameters was determined on the basis of 26 stations located throughout the strait (Figure 4), where "surface" refers to samples collected from a depth of 1m. A suite of samples was also collected from a depth of 5m during Cruise 78-07. Complete depth profiles were obtained at Stations 1, 3, 15, and 25. Furthermore, Station 15 was investigated on nine other occasions during the study period in order to determine how dissolved manganese concentrations varied off the river mouth. Data for dissolved and suspended particulate constituents are tabulated in Appendices B.1 and B.2, respectively.

5.2 Surface Distribution of Manganese

Some difficulties exist in the interpretation of the data for surface waters in the Strait of Georgia. The data are not synoptic as two days were required to complete the sampling programme. The wind affects both the circulation and mixing processes within the brackish surface layer. Therefore, due to short term variations in the wind pattern, the distribution of

water parameters in the surface layer will tend to show the mixed effects of all conditions existing during the cruise.

The Fraser River acts as the major source of fresh water for the Strait of Georgia (Waldichuk, 1957). This is evident in the distribution of salinity in surface waters (Figures 25a through 28a). Lowest salinities tend to be associated with stations in the vicinity of Sand Heads. The salinity increases to the northwest and southeast of this area; however, these trends are not necessarily regular for reasons outlined previously. Furthermore, data from Station 7 show depressed salinities indicating the influence of the Squamish River and/or the North Arm of the Fraser River (Figure 2) during summer months.

Salinities in the surface waters were high, falling in the range of 27.989 to 30.316 ppt, throughout the Strait of Georgia in January 1979 (Figure 27a). This resulted from intense wind mixing and low Fraser River runoff at this time. Wind speeds of 50 to 60 knots were recorded during the cruise. In contrast, the lowest salinities were observed in May 1979 (Figure 28a). This cruise coincided with maximum discharge rates of the Fraser River during a sampling period (Figure 3).

The surface distribution of dissolved manganese is determined almost exclusively by the salinity (Figures 25b through 28b). The same holds true for samples collected from a depth of 5m during Cruise 78-07 (Figure 26d). The Fraser River is the major source of dissolved manganese for surface waters in the Strait of Georgia. Accordingly, the highest concentrations were observed in the vicinity of Sand Heads. Dissolved

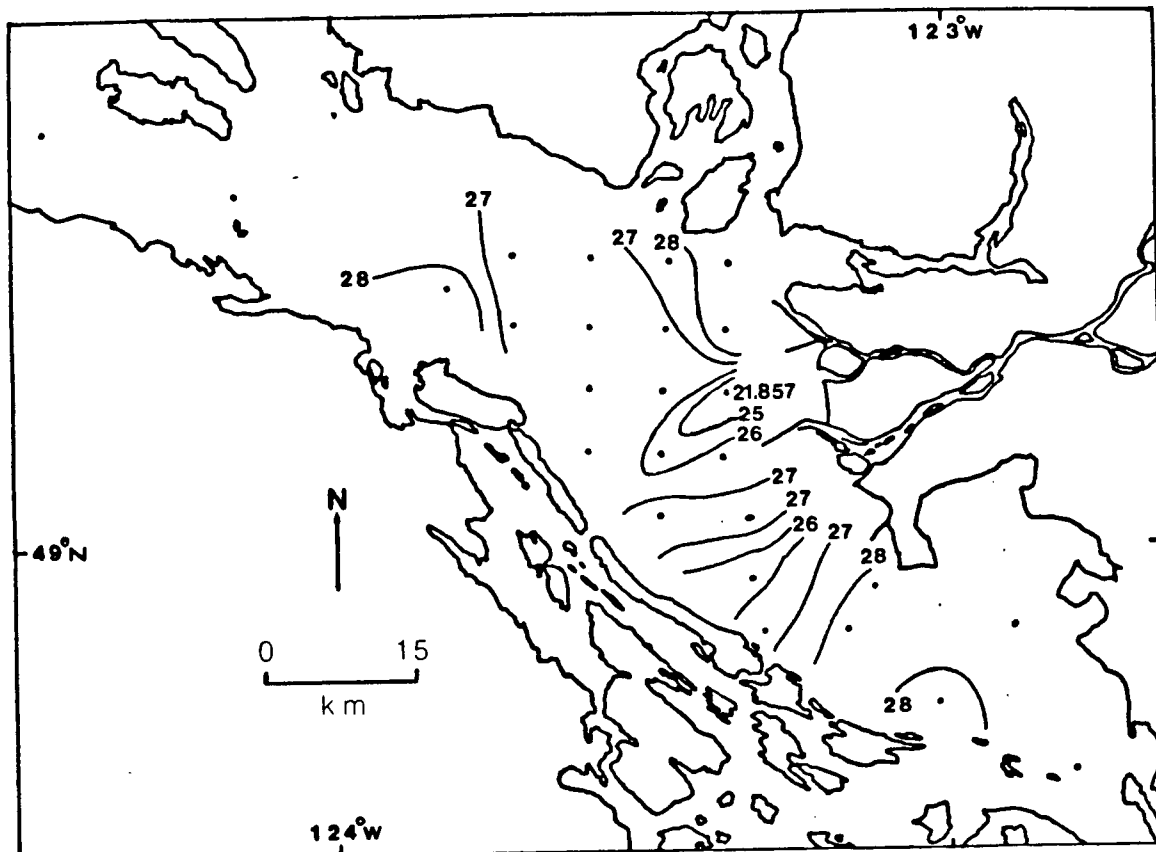


Figure 25a Salinity (ppt)

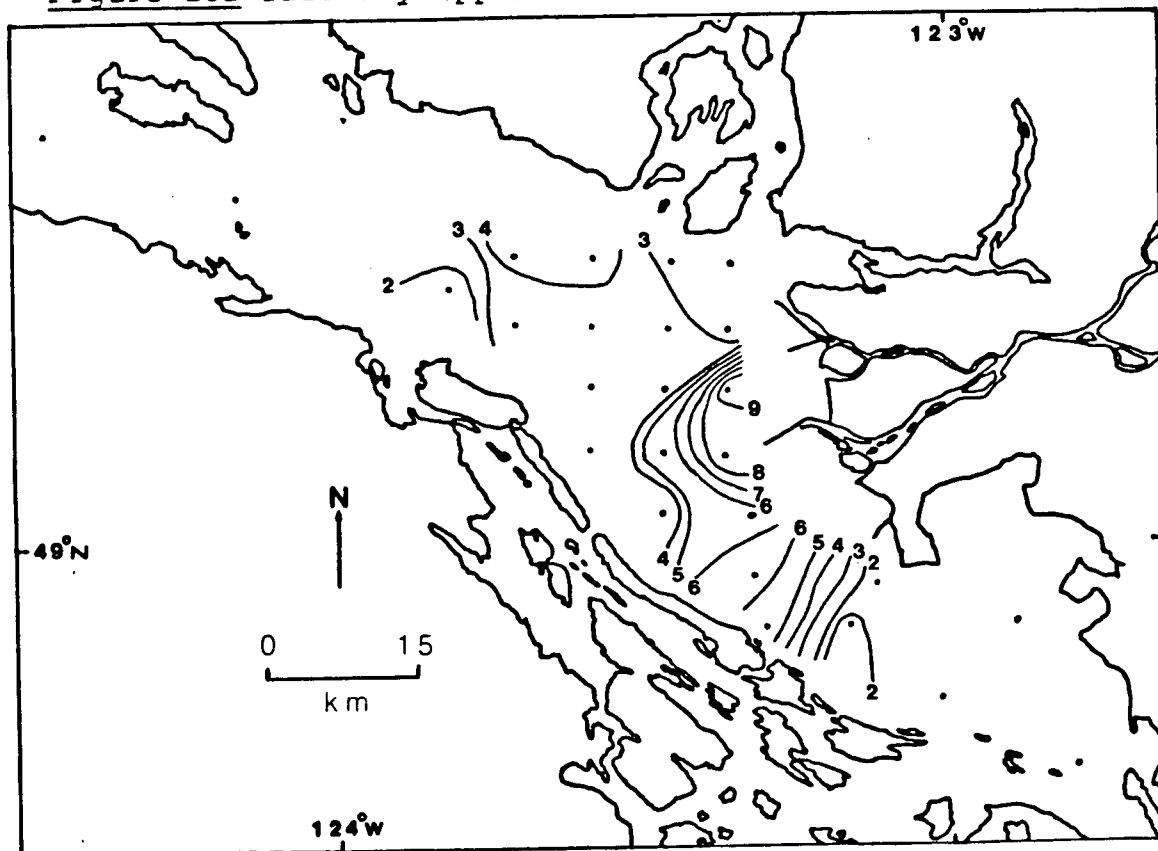


Figure 25b Dissolved manganese (ppb)

FIGURE 25 Surface distribution of salinity and dissolved manganese in the Strait of Georgia during Cruise 78-01.

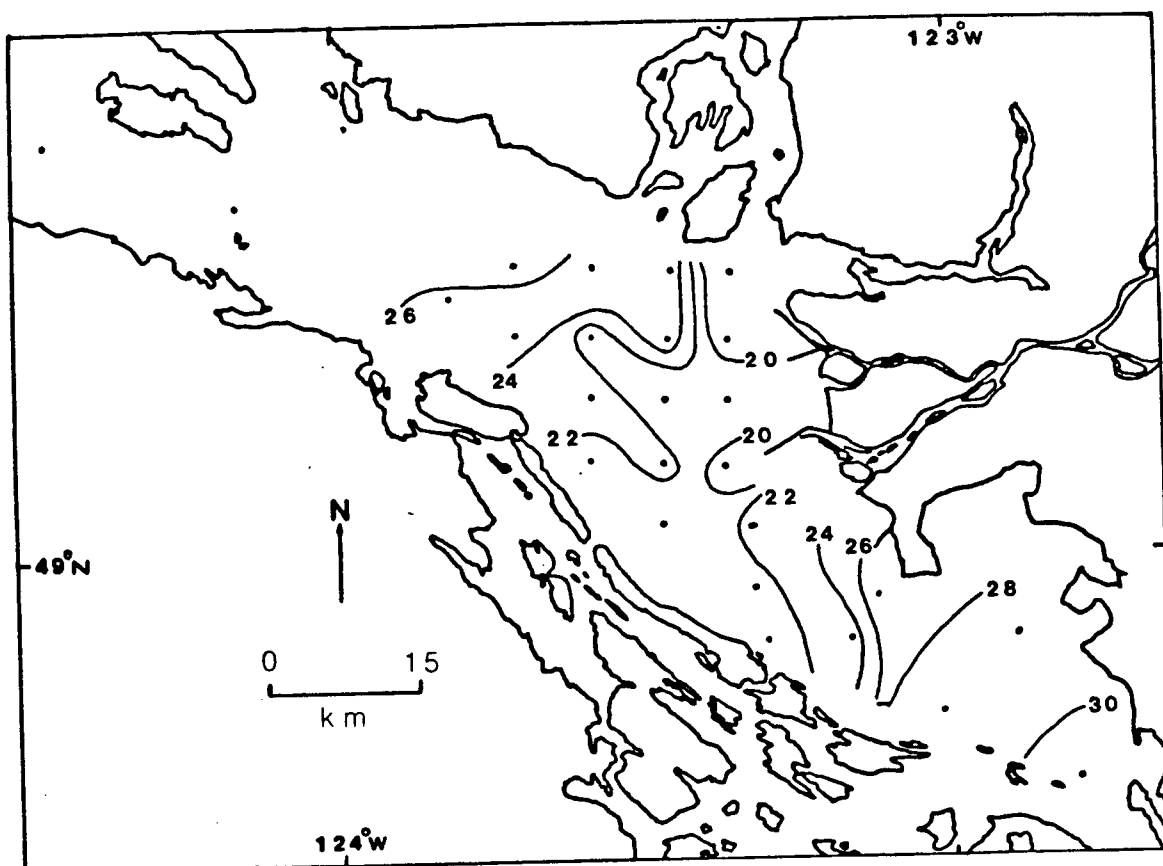


Figure 26a Salinity (ppt), 1 m

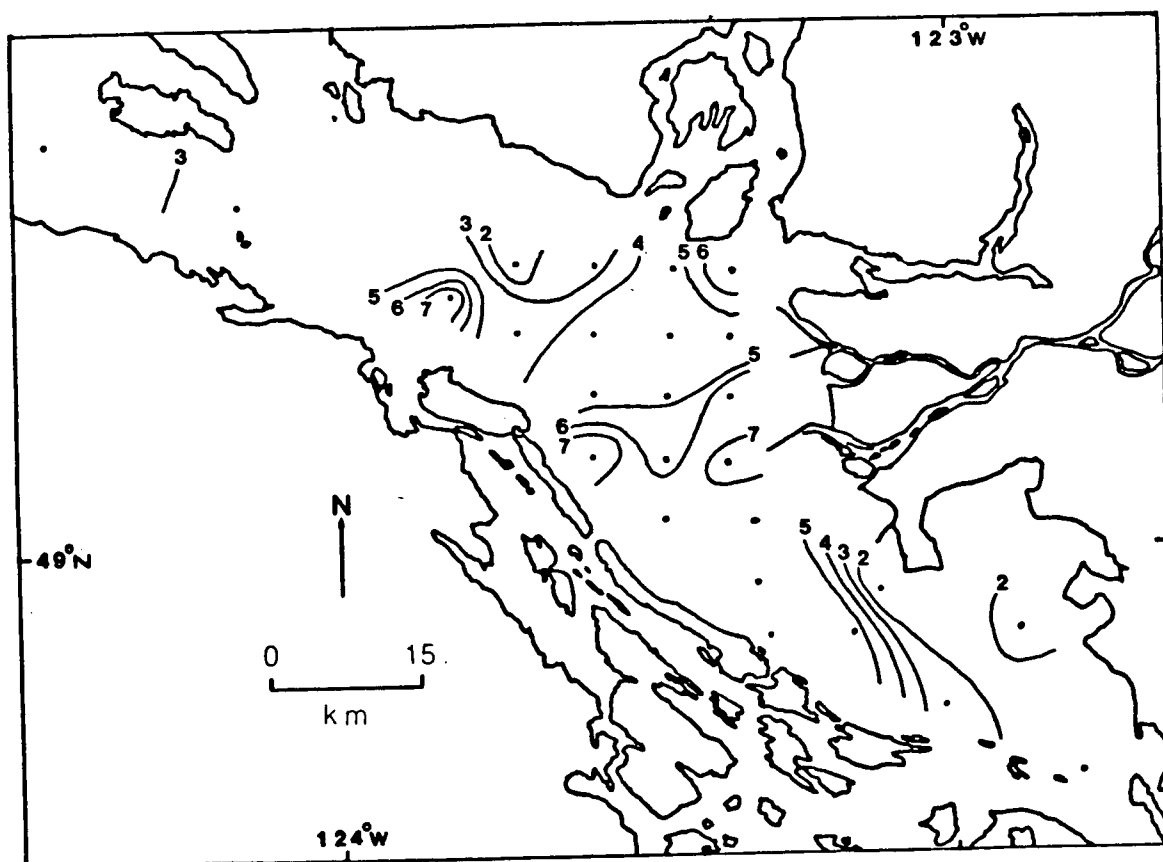


Figure 26b Dissolved manganese (ppb), 1 m

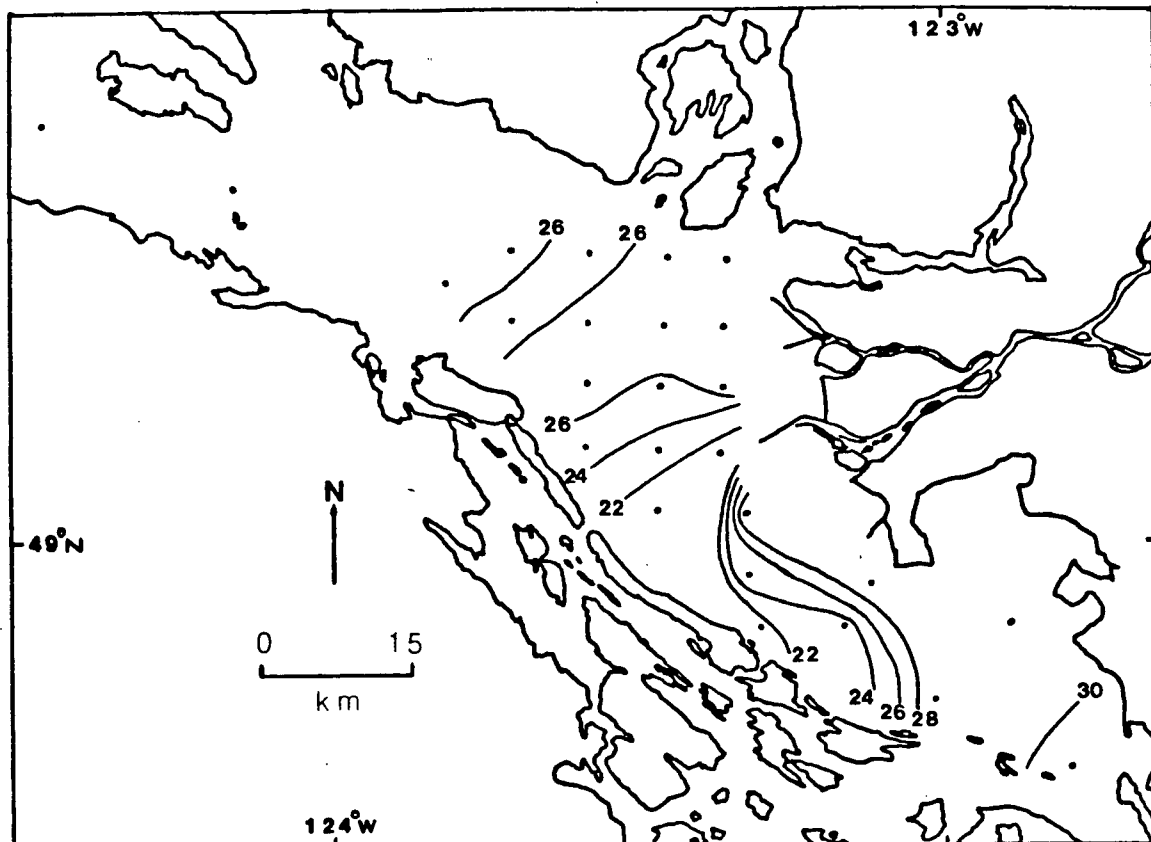


Figure 26c Salinity (ppt), 5 m

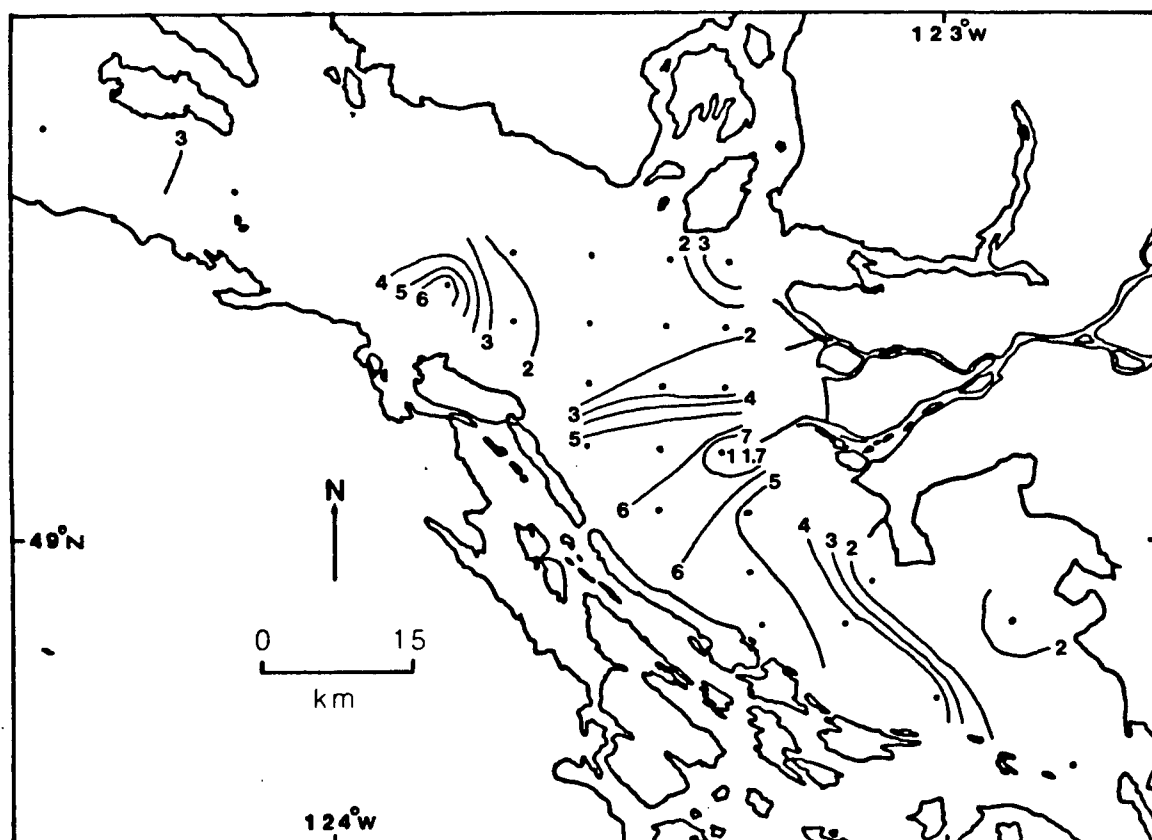


Figure 26d Dissolved manganese (ppb), 5 m

FIGURE 26 The distribution of salinity and dissolved manganese in the Strait of Georgia at 1 and 5 m, Cruise 78-07.

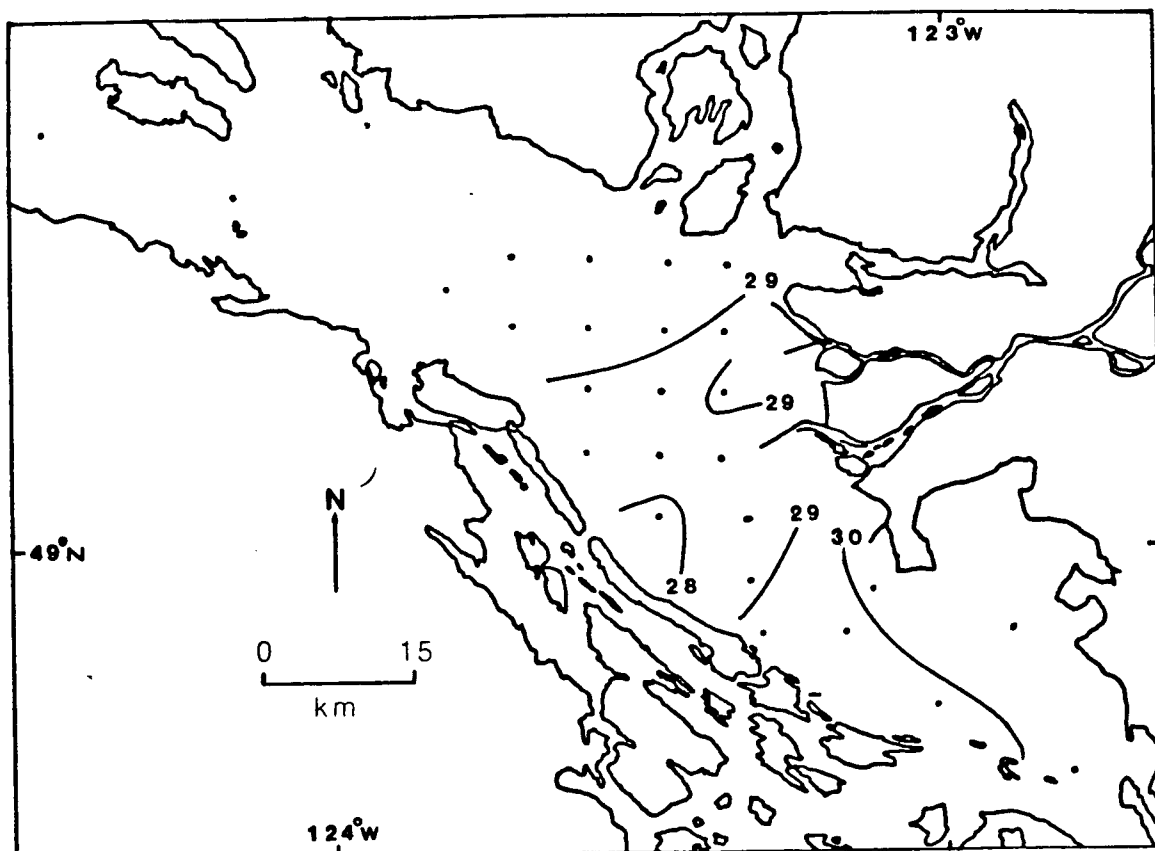


Figure 27a Salinity (ppt)

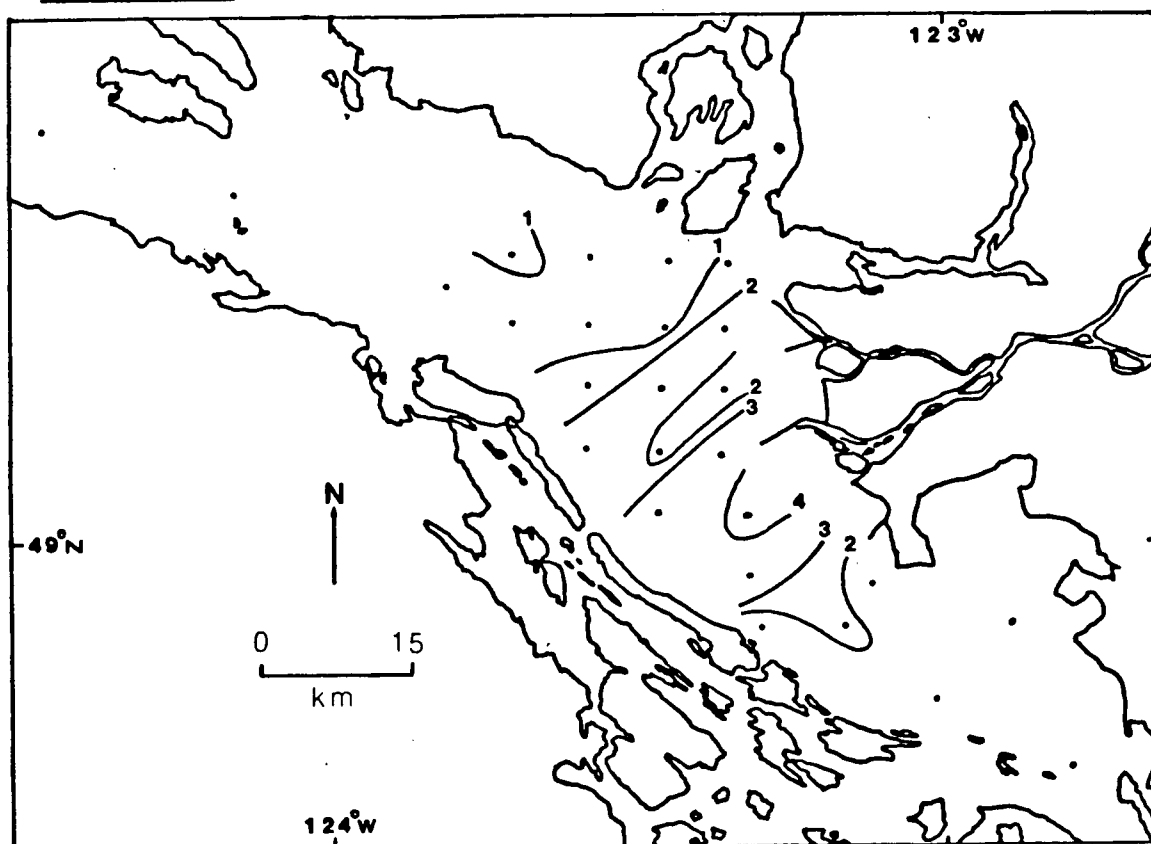


Figure 27b Dissolved manganese (ppb)

FIGURE 27 Surface distribution of salinity and dissolved manganese in the Strait of Georgia during Cruise 79-01.

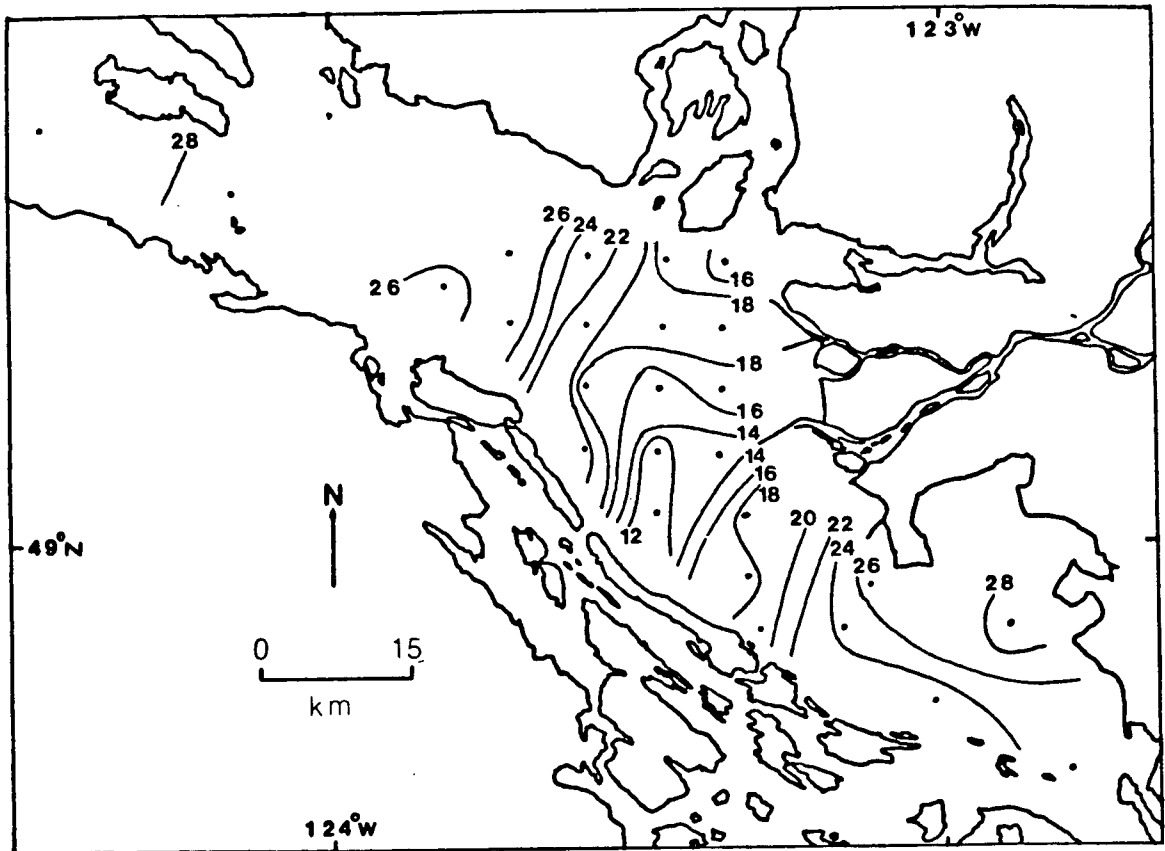


Figure 28a Salinity (ppt)

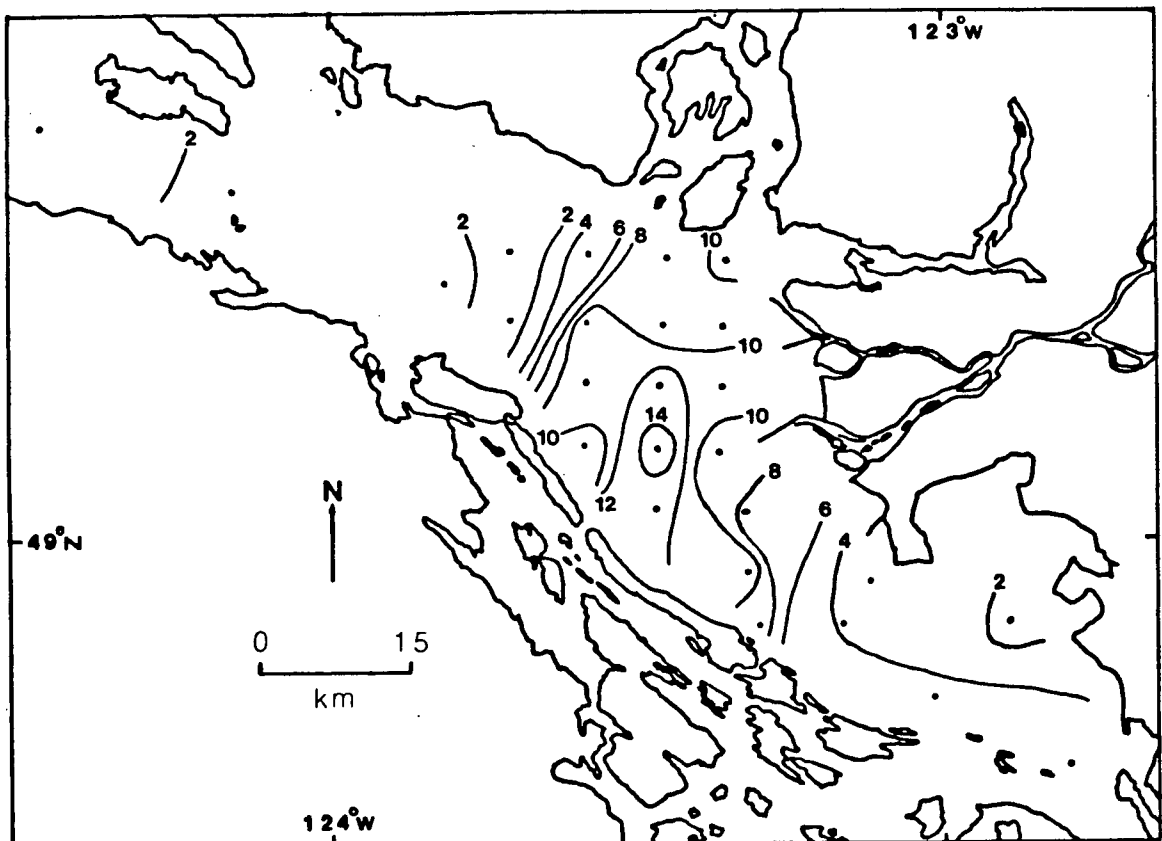


Figure 28b Dissolved manganese (ppb)

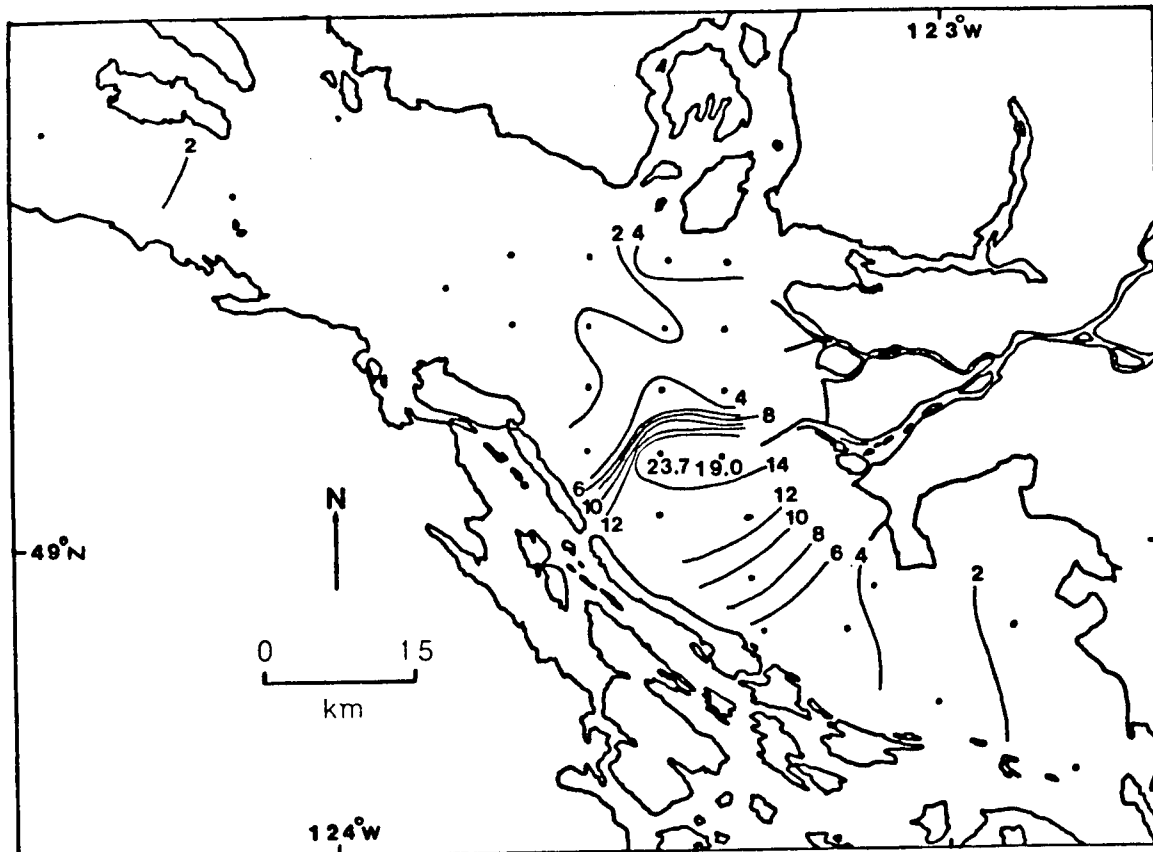


Figure 28c Suspended particulate manganese (ppb)

FIGURE 28 Surface distribution of salinity, dissolved manganese, and suspended particulate manganese in the Strait of Georgia during Cruise 79-12.

manganese levels generally decreased with distance from the river mouth, that is, they decreased with an increase in salinity.

Data for Station 7 indicate a secondary source of dissolved manganese during the summer (Figures 26b and 28b). This source may be associated with water from Burrard Inlet (Figure 4), but more probably originates in the discharge from either the Squamish River or the North Arm of the Fraser River.

Station 3 also indicates a localized source of dissolved manganese, but this was evident during Cruise 78-07 only (Figure 26b). In comparison to waters of similar salinity at other locations, the waters at Station 3 were enriched with dissolved

manganese to a depth of 10m. The source of this manganese is unknown.

Intense mixing in January 1979 resulted in fairly low levels of dissolved manganese (Figure 27b). Values of 1.36 ppb were measured in the southern portions of the Strait of Georgia but concentrations less than 1 ppb were observed near Texada Island. In contrast, the highest dissolved manganese concentrations occurred in May 1979, corresponding to periods of high Fraser River discharge rates and hence low salinities throughout the Strait of Georgia (Figure 28b).

During Cruise 79-12, the dilution of Fraser River water to the northwest and southwest generates two distinct mixing curves for the dissolved manganese. These trends are evident in the plot of dissolved manganese versus salinity (Figure 29). For salinity values greater than 25 ppt, the upper curve represents dilution in the southern portions of the Strait of Georgia while the lower curve is associated with the northern stations near Texada Island. Thus, the sea water end members at either extreme of the Strait of Georgia have different dissolved manganese concentrations. This will be examined in Section 5.4.

The surface distribution of suspended particulate manganese was determined for Cruise 79-12 only. While select samples from other cruises were analyzed, concentrations were consistently less than 0.5 ppb. As these values approach the detection limit, analyses throughout the Strait of Georgia were performed only on samples from Cruise 79-12 when high river discharge rates resulted in measureable manganese concentrations.

Suspended particulate manganese levels mimic the dissolved

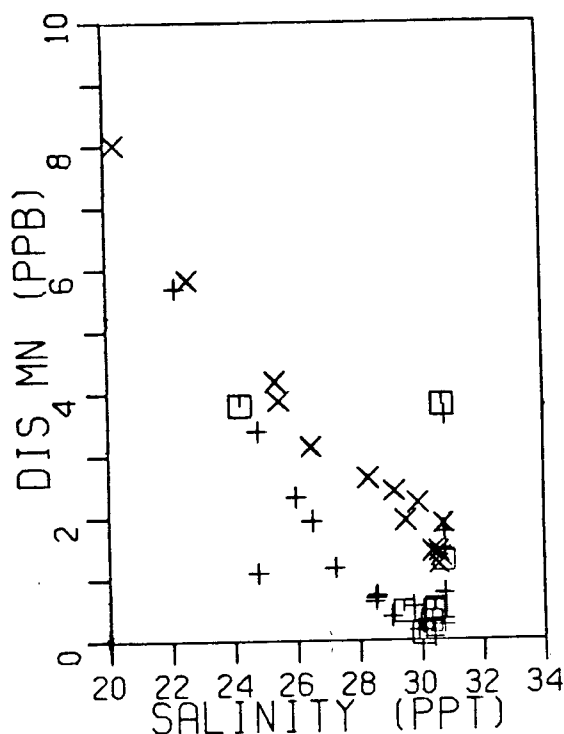


FIGURE 29 Dissolved manganese concentrations plotted versus salinity, for samples from Cruise 79-12 with salinities greater than 20 ppt only. Symbols: \square Station 15, + northern stations, X southern stations.

manganese values reflecting their common source (Figure 28c). However, the suspended particulate Mn:Al ratio increased with increasing salinity (Figure 20e). This could result from the oxidative precipitation of dissolved manganese and/or the relatively rapid settling of suspended particulate material with low manganese content.

The data cannot specifically indicate which of these processes may be occurring. While significant oxidative precipitation of manganese was not observed in the Fraser Estuary, this process could occur in the Strait of Georgia during the summer due to the longer residence time of the water together with high dissolved oxygen concentrations (Figure 7d) and pH values near 8.5 (Figure 8d). Furthermore, the oxidative

precipitation onto the surfaces of clay minerals may result in fine-grained material having a higher Mn:Al ratio than coarse-grained sediment. Subsequent settling of the coarser material could lead to a decrease in the absolute concentration of manganese but an increase in the suspended particulate Mn:Al ratio. Vertical profiles in the Gulf of St Lawrence indicate that such differential settling processes develop a suspended particulate manganese-rich layer some distance above the sediment/water interface (Sundby, 1977; Yeats et al., 1979).

5.3 Time Series at Station 15

The dissolved manganese data for Station 15 are illustrated in Figure 30. The bottom depth differs due to variations in station location.

The data indicate a source of dissolved manganese for both the surface and bottom waters. Manganese in the surface water is derived from the Fraser River. Variations in the dissolved manganese concentrations in these waters occur due to differences in both the salinity at the time of sampling and the mean dissolved manganese content of the Fraser River.

Elevated dissolved manganese concentrations in the bottom waters indicate a flux of manganese from the sediment. In this case, variations in the manganese content may be associated with the length of time that the water was in contact with the sediments. A series of samples collected near the bottom during Cruises 79-07 and 79-12 shows that significant enrichment occurs in waters within 20 m of the sediments.

At intermediate depths, the dissolved manganese

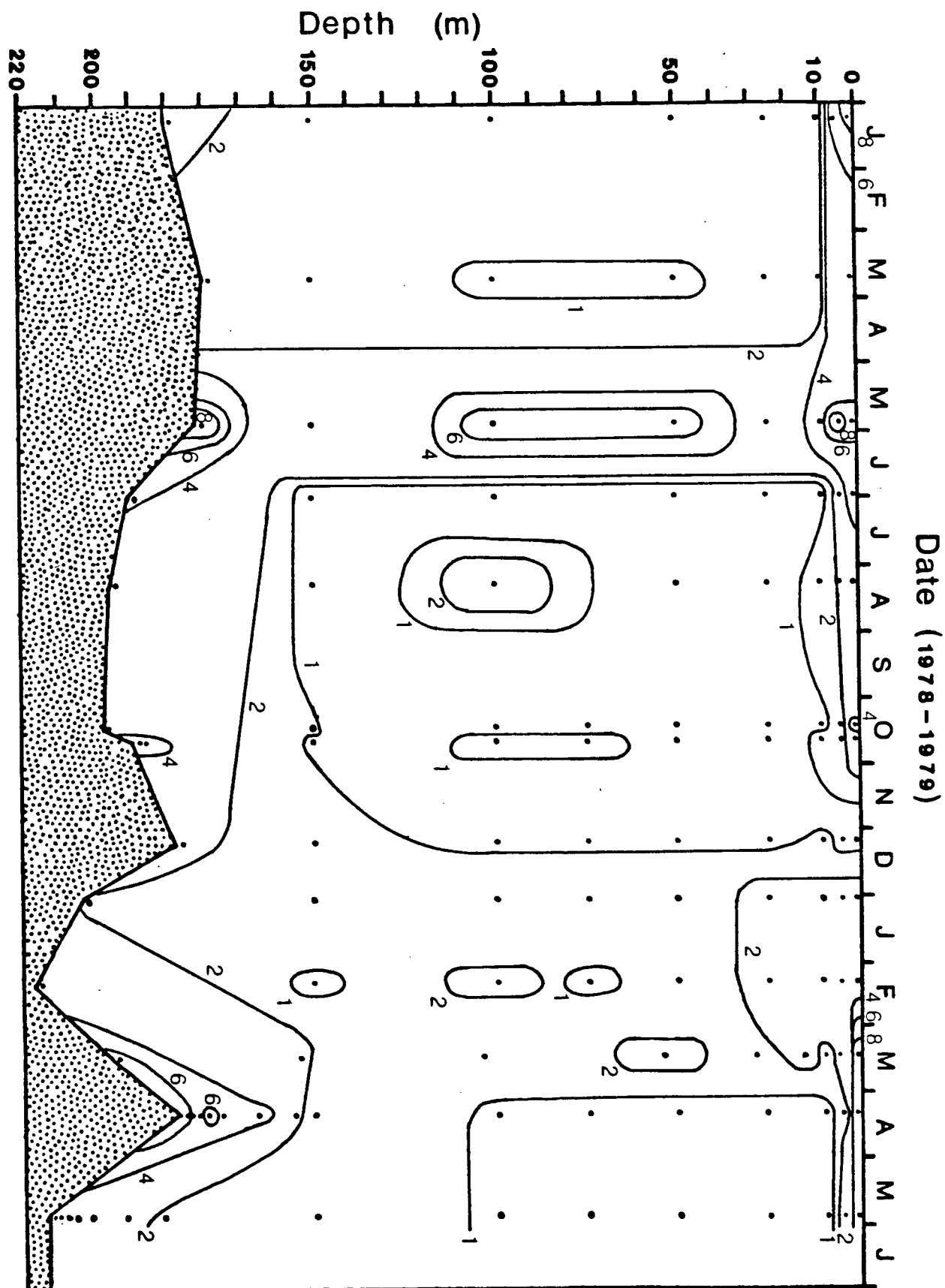


FIGURE 30 Time series of dissolved manganese concentrations at Station 15 from January 1978 to June 1979.

concentrations exhibit seasonal variations. Levels tend to be higher in the winter months than during the summer due to variations in the stability of the water column. The development of a pycnocline between 10 and 20 m in the summer leads to the formation of a surface brackish layer which is manganese-rich and exits the Strait of Georgia via the southern channels. Waters at mid-depths have uniformly low dissolved manganese concentrations due to mixing processes below the pycnocline. Depletion may be enhanced due to oxidative precipitation of dissolved manganese. However, intensive mixing during the winter causes higher mid-depth manganese levels.

The elevated manganese concentrations observed at 50 and 100 m depths in May 1978 do not conform to this seasonal pattern. While the reason for this anomaly is unknown, the profile could be generated if the water from intermediate depths was horizontally advected from a local sediment/water interface where the manganese concentration had been enhanced due to diffusion from the underlying sediments.

Vertical profiles of suspended particulate manganese were obtained during Cruises 78-16 and 79-07 (Figure 31) in October and April, respectively. The profiles were similar both in form and concentrations except for two values. Firstly, variations in the suspended particulate manganese level in surface waters occurred due to salinity differences. The lower concentration in October (1.6 ppb) was associated with a salinity of 24 ppt, compared to 5.4 ppb and a salinity of 10 ppt in April. Secondly, the suspended particulate manganese content was 4.4 ppb at 150 m in April. This anomalous sample may be indicative

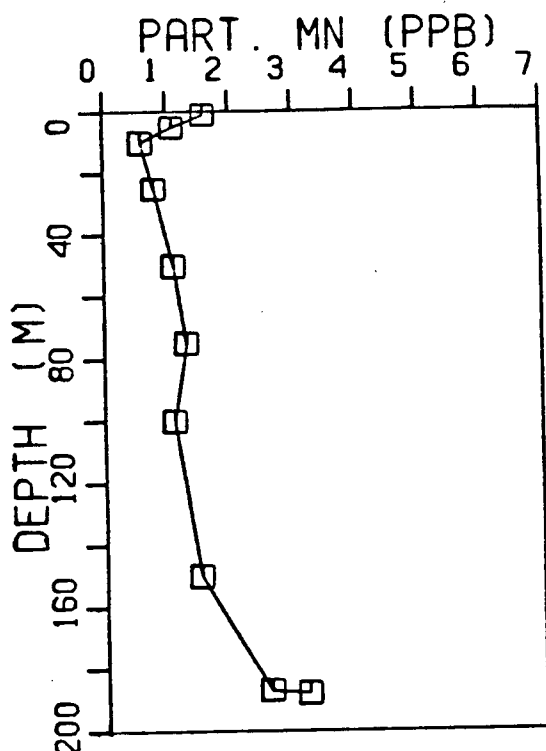


Figure 31a Cruise 78-16

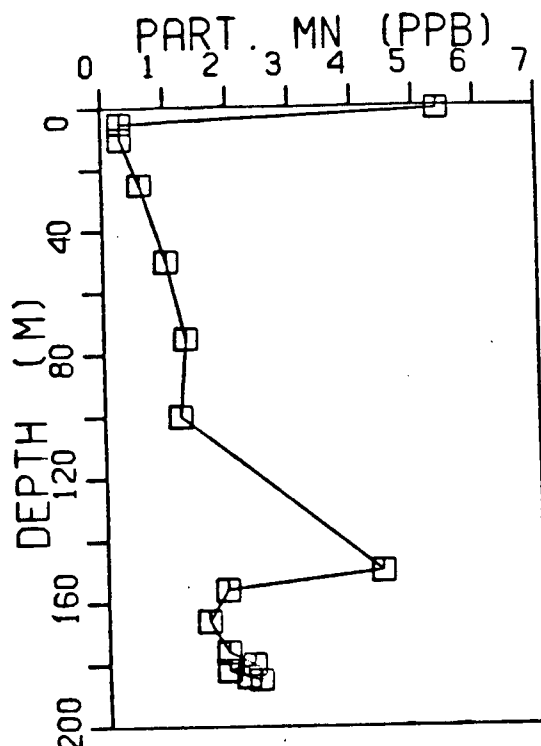


Figure 31b Cruise 79-07

FIGURE 31 Profiles of suspended particulate manganese concentrations for Station 15, Cruises 78-16 and 79-07.

of short term fluctuations in the rate of sediment discharge from the Fraser River. Alternatively, this water may have been advected from a local sediment/water interface where bottom sediments had been resuspended.

As previously mentioned, elevated dissolved manganese concentrations in bottom waters at Station 15 indicate a flux of manganese from the bottom sediments. Cores were obtained from Station 15 during Cruises 78-01 and 79-02. The profiles of dissolved manganese in the interstitial waters (Figure 32) exhibit concentrations in the ppm range with a subsurface maximum at a depth of 3 to 6 cm. These characteristic profiles indicate the reduction of manganese oxides at depth due to anoxic conditions (Li et al., 1969; Holdren et al., 1975).

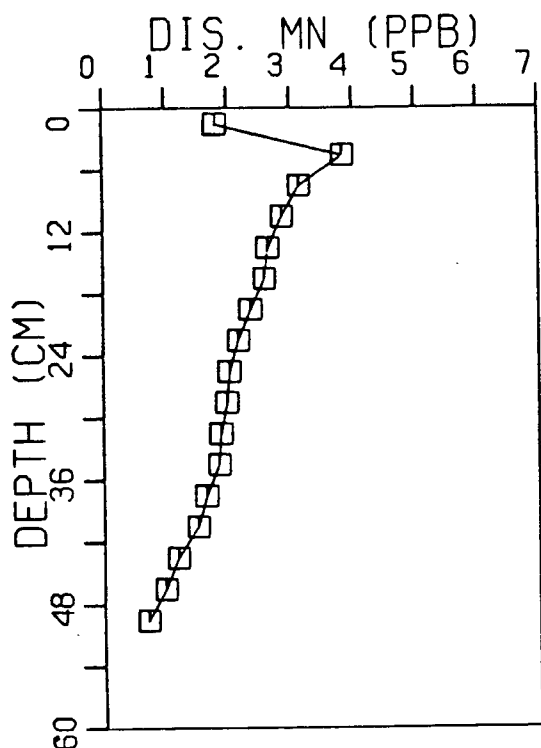


Figure 32a Cruise 78-01

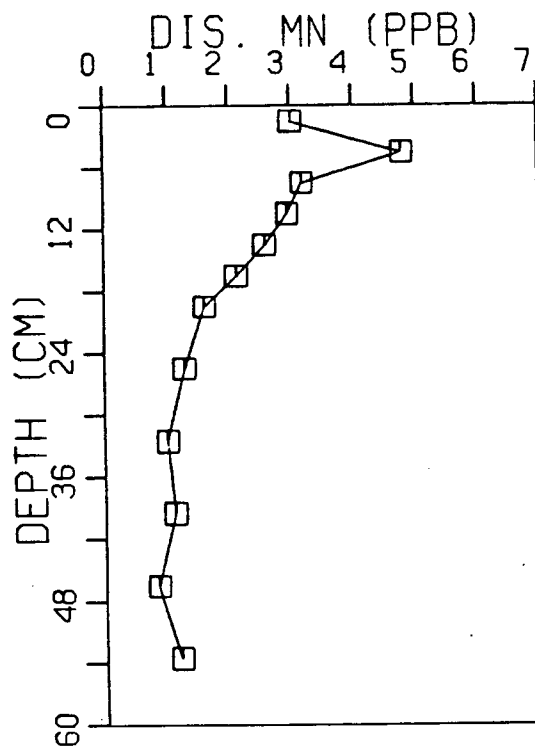


Figure 32b Cruise 79-02

FIGURE 32 Profiles of dissolved manganese concentrations in interstitial waters of sediments from Station 15, Cruises 78-01 and 79-02.

Soluble manganous ion may be introduced into overlying waters due to the resuspension of sediments and/or molecular diffusion.

5.4 Profiles at Stations 1, 3, and 25

Depth profiles of dissolved manganese were obtained at Stations 1, 3, and 25. Profiles at the northern locations were similar and showed little seasonal variations. Figure 33a illustrates a representative example from Station 3. While the concentrations of dissolved manganese at mid-depths were low (less than 1 ppb), bottom waters exhibited enhanced levels due to diagenetic processes in the sediments. The flux of manganese from the sediments enriched waters 50 m above the bottom.

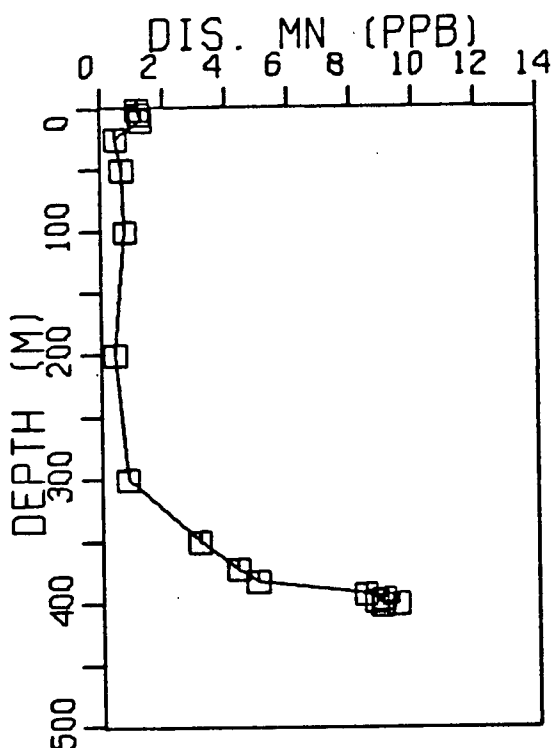


Figure 33a Dissolved Mn

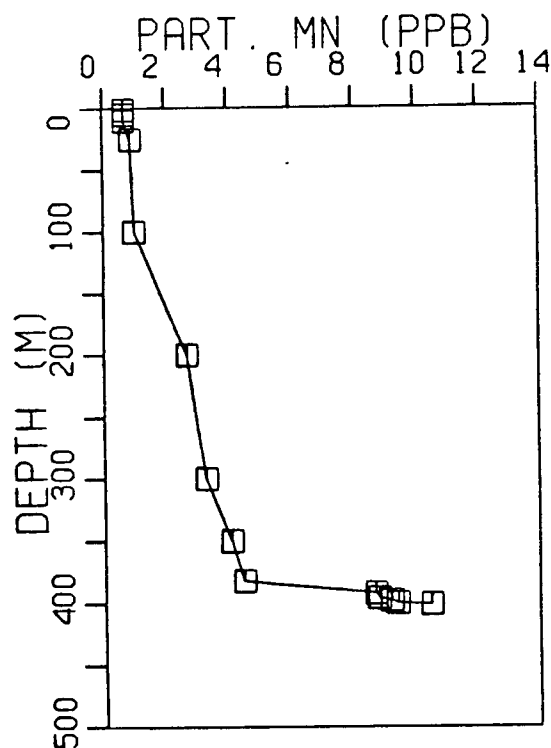


Figure 33b Particulate Mn

FIGURE 33 Profiles of dissolved and suspended particulate manganese concentrations for Station 3, Cruise 79-07.

The concentrations of suspended particulate manganese steadily increased with depth at this time (Figure 33b). Again, the data do not clearly indicate whether this results from the oxidative precipitation of manganese in situ and/or the resuspension of bottom sediments. These fine-grained sediments have a higher Mn:Al ratio than observed for estuarine sediments (Table IX). It is worth noting that this area is a known site of manganese nodule formation in the Strait of Georgia.

Concentrations of dissolved manganese in the water column at Station 25 (Table X) were generally higher than those observed in the northern portion of the strait. Levels below 1.0 ppb were observed only in February 1979. Bottom samples suggest that there may be a significant flux of manganese from

TABLE X Dissolved Manganese Data from Station 25.

	Dissolved Manganese Concentrations (ppb)			
Depth (m)	78-01	78-07	79-02	79-12
1	2.81	2.43	1.10	5.83
5	2.64	2.86	0.87	2.62
10	1.39	1.69	0.46	2.41
25	2.81	1.55	0.46	1.94
50	1.72	1.41	0.46	1.44
75	----	----	0.23	1.23
100	1.76	0.99	0.14	1.44
150	1.37	1.02	0.14	1.36
Bottom	1.55	2.09	0.09	1.89

the sediments. This secondary source of manganese, coupled with intense vertical mixing due to the proximity of Boundary Passage (Figure 4), may cause the relatively high dissolved manganese levels observed at mid-depths. Similarly, such processes may be manifest in the different manganese dilution curves observed during Cruise 79-12. In Figure 29, the mixing of Fraser River water in the northern section of the Strait of Georgia (lower curve) can be distinguished from mixing processes south of the river mouth (upper curve). Samples with salinities above 30 ppt and manganese concentrations greater than 3 ppb were collected 1 m above the bottom.

5.5 Summary

The distribution of dissolved manganese in the surface waters of the Strait of Georgia indicates that the Fraser River is the major source of this metal. Concentrations are determined largely by the dilution of the river discharge. Secondary sources of manganese were observed during the summer at Station 7 (possibly Squamish River discharge) and Station 3.

Bottom waters have enhanced dissolved manganese concentrations due to reductive remobilization of manganese from the sediments. Thus, the Strait of Georgia is similar to the Gulf of St. Lawrence since bottom sediments act as a significant source of dissolved manganese.

Concentrations of dissolved manganese at mid-depths are determined by variations in the stability of the water column. Levels are depleted below the pycnocline during the summer but intense winter mixing causes enhanced concentrations. Similarly, tidal mixing in the southern passages causes enhanced dissolved manganese concentrations at mid-depths even during the summer. These processes may be manifest in the dilution curves for dissolved manganese which differ for Fraser River mixing processes in the northern and southern extremes of the Strait of Georgia.

Finally, profiles of suspended particulate manganese indicate increasing concentrations with depth. This may result from the oxidative precipitation of manganese and/or the resuspension of bottom sediments.

6. CONCLUSIONS AND FUTURE WORK

The Fraser Estuary was investigated five times under varying flow regimes. A maximum dissolved manganese concentration was consistently observed in the initial mixing zone. The specific salinity of this peak varied from one cruise to the next but appeared to be independent of the Fraser River discharge rate. Two potential sources of this excess manganese were examined, namely, riverborne suspended material and estuarine bottom sediments.

While the possibility cannot be ruled out that dissolution or desorption of manganese from riverborne suspended particulates may be significant during the freshet, this would seem an unlikely mechanism to account for the manganese enrichment observed at other times of the year. Experimental evidence indicates that dissolved manganese concentrations in mixtures of fresh and saline waters agree with results anticipated from physical mixing processes alone. River sediment suspended in estuarine water released only 1.7 ppm manganese on a dry weight basis, insufficient to account for the dissolved manganese peak in the Fraser Estuary as suspended sediment loads often fall in the range of 10 to 24 mg/l. A geochemical mass balance between riverborne suspended particulate manganese and estuarine "excess" dissolved manganese cannot be attained at some times of the year, even with complete dissolution of all the suspended particulate manganese. Suspended particulate manganese behaves conservatively in the initial mixing zone and the suspended particulate Mn:Al ratio does not change significantly in the estuary. The concentration

of total manganese also exhibits a maximum at low salinity on at least two occasions. Finally, because the Fraser Estuary remains well-oxygenated, the reductive dissolution of manganese oxides associated with riverborne suspended particulates is not favoured thermodynamically.

The field data suggest that the excess dissolved manganese observed in the surface waters may be derived from estuarine bottom sediments. Throughout the year the concentration of dissolved manganese in the salt wedge exceeds levels in surface waters of comparable salinity. Enhanced manganese content in the bottom waters appears to be coupled to the tidal resuspension of sediments in the Fraser Estuary. While desorption (or dissolution) from these resuspended sediments must be primarily responsible, manganese enrichment may also be influenced to a lesser extent by the release of interstitial waters having high concentrations of dissolved manganese due to in situ reduction of amorphous manganese oxides. The occurrence of these processes is suggested by a general downstream decrease in the ammonium oxalate extractable manganese content in estuarine surficial sediments, together with Mn:Al ratios in these sediments lower than observed in riverborne suspended particulates. Furthermore, the calculated bedload required to achieve mass balance of manganese in the system agrees with estimates of bedload transport in the Fraser Estuary (Pretious, 1972).

The distribution of dissolved manganese in the surface waters of the Fraser Estuary consists of two conservative dilution curves which intersect at the salinity and manganese

concentration corresponding to the dissolved manganese maximum. The water properties of this peak are determined by the mixing of river water with saline water from the toe of the salt wedge. The entrainment of this bottom water establishes the conservative mixing curve observed at low salinities in the surface waters. The dilution curve in the high salinity region results from the subsequent mixing between the sea water end member and the manganese maximum at low salinity.

Despite being supersaturated with respect to manganese dioxide, surface waters in the lower reaches of the estuary did not exhibit removal of dissolved manganese. Furthermore, the suspended particulate manganese also behaved conservatively in this region and suspended particulate Mn:Al ratios remained relatively constant. The oxidative precipitation of manganese may be undetected due to the short residence time of waters in the Fraser Estuary.

Throughout the year the alkalinity behaves conservatively through most of the salinity range in the estuary. Anomalous behaviour at low salinities may be attributed to the removal of alkalinity; however, errors in the technique at these low ionic strengths may tend to exaggerate the extent of removal.

Except during the freshet, the dissolved oxygen also behaves conservatively in the Fraser Estuary. The oxygen undersaturation calculated for salt wedge waters results from the horizontal advection of oxygen-depleted water from outside the estuary. During the summer months the concentration of dissolved oxygen in estuarine waters is modified by biological processes.

The distribution of pH with respect to salinity in the surface waters displays a pH minimum in the initial mixing zone which persists throughout the year. This has been attributed to variations in the salinity dependence of the dissociation constants of carbonic acid (Mook and Koene, 1975). However, the observed pH minimum can be replicated by the model of Mook and Koene (1975) only when mixing in the surface waters of the estuary is considered as a two stage process. Finally, the low and relatively uniform pH values observed in the salt wedge waters are consistent with the horizontal advection of oxygen depleted waters from outside the Fraser Estuary.

Data from the Strait of Georgia were collected during a seventeen month sampling period extending from January 1978 until May 1979. The alkalinity behaved conservatively in the Strait of Georgia throughout this time period. The pH and dissolved oxygen concentrations displayed seasonal variations related to primary productivity and mixing processes.

The distribution of dissolved manganese in the surface waters indicated that the Fraser River is the major source of this metal for the Strait of Georgia. Concentrations are determined mainly by the dilution of the Fraser River discharge in the strait. Bottom waters have enhanced dissolved manganese concentrations due to reductive remobilization of manganese from the sediments. Concentrations of dissolved manganese at mid-depths are determined by seasonal variations in the stability of the water column.

Depth profiles of suspended particulate manganese indicate increasing concentrations with depth. This may result from the

oxidative precipitation of manganese and/or the resuspension of bottom sediments.

As a consequence of the results presented, three avenues of future research can be suggested. Firstly, data indicate the possible removal of alkalinity in the initial mixing zone. More appropriate analytical techniques might be employed to resolve the behaviour of alkalinity at low salinities. Secondly, manganese has been shown to behave conservatively in the Fraser Estuary. Manganese enrichment in surface waters may be influenced by diagenetic processes within the estuarine sediments. Accordingly, these sediments should be examined in greater detail, particularly to determine the position of anoxic zones in relation to those sediments influenced by waters of the salt wedge. Thirdly, hydrous manganese oxides may influence the concentrations of several metals (Co, Cu, Ni, Pb, and Zn) in natural waters (Jenne, 1968; Hem, 1978). Since the desorption or dissolution of manganese from estuarine bottom sediments causes significant enrichment in surface waters, similar enhancement of other metals might be anticipated. The distribution of such metals in both the waters of the salt wedge and interstitial waters of estuarine sediments should be determined in order to establish the extent to which their chemistries may be coupled to that of manganese in the Fraser Estuary. However, as demonstrated in this work, the estuarine chemistry of trace metals can be determined only when dissolved and suspended particulate components are examined in conjunction with the sediments.

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APPENDIX A Summary of Station Positions and Sampling Programme

APPENDIX A.1 Station Positions in the Strait of Georgia

Station Number	North Latitude	West Longitude
1 ⁽¹⁾	49° 26.0'	124° 27.5'
2	49° 21.8'	124° 09.0'
3 ⁽¹⁾	49° 16.6'	123° 48.4'
4	49° 18.5'	123° 42.0'
5	49° 18.5'	123° 34.0'
6	49° 18.5'	123° 27.5'
7	49° 18.5'	123° 21.5'
8	49° 14.2'	123° 21.5'
9	49° 14.2'	123° 27.5'
10	49° 14.2'	123° 34.0'
11	49° 14.2'	123° 42.0'
12	49° 09.9'	123° 34.0'
13	49° 09.9'	123° 27.5'
14	49° 09.9'	123° 21.5'
15 ⁽¹⁾	49° 05.6'	123° 21.8'
16	49° 05.6'	123° 27.5'
17	49° 05.6'	123° 34.0'
18	49° 01.3'	123° 27.5'
19	49° 01.3'	123° 18.5'
20	48° 57.0'	123° 18.5'
21	48° 54.4'	123° 18.2'
22	48° 57.2'	123° 07.0'
23	48° 54.2'	123° 09.0'
24	48° 54.5'	122° 53.5'
25 ⁽¹⁾	48° 49.5'	123° 01.0'
26	48° 45.2'	122° 48.0'

(1) Complete depth profile taken at these stations

APPENDIX A.2 Station Positions in the Fraser Estuary

Station Number	North Latitude	West Longitude
50	49° 06.00'	123° 20.0'
51	49° 06.00'	123° 19.30'
52	49° 06.00'	123° 18.78'
53	49° 06.25'	123° 18.00'
54	49° 07.18'	123° 16.00'
55	49° 07.93'	123° 14.0'
56	49° 07.44'	123° 12.0'
56.3	49° 07.00'	123° 11.2'
57	49° 06.60'	123° 09.6'
58	49° 06.45'	123° 07.55'
58.3	49° 06.60'	123° 07.45'
59	49° 06.85'	123° 05.5'
60	49° 07.85'	123° 03.85'
61	49° 08.90'	123° 02.0'
62	49° 09.35'	123° 00.1'
63	49° 09.30'	122° 57.1'
64	49° 10.32'	122° 55.35'
65	49° 12.28'	122° 53.88'
67	49° 12.70'	122° 53.20'
70	49° 10.8'	122° 34.0'

APPENDIX A.3 Water Sampling Programme

Cruise	Dates	Ship	Strait of Georgia	Fraser Estuary	Stn 15
	1978				
78-01	Jan 9-12	CFAV Endeavour	X		X
78-04	Mar 22	CSS Vector		X	X
78-07	May 29-30	CFAV Endeavour	X		X
78-10	Jun 30	CSS Vector			X
78-11	Jul 19	Brisk		X	
78-12	Aug 10	CSS Vector			X
78-13	Sep 21	CSS Vector	Stn 1		
78-16	Oct 16-20	CSS Vector		X	X
78-20	Dec 5	CSS Vector			X
	1979				
79-01	Jan 2-5	CSS Vector	X	X	X
79-02	Feb 6	MV Pandora II	Stn 25		X
79-05	Mar 13	CSS Vector			X
79-07	Apr 4-5	CSS Parizeau	Stn 3		X
79-12	May 28-31	CSS Vector	X	X	X

APPENDIX A.4 Sediment Sampling Programme

Collection	Date	Station Number	Depth (m)	Salinity (ppt)
Shipek Grab	Jan 12/78	51	100	29.925
		52	50	29.825
	May 28/79	3	420	30.939
	May 29/79	15	212	30.714
	May 30/79	53	35	30.027
		54	13	28.143
		55	11	0.0
		56	11	0.0
		59	11	0.0
		65	11	0.0
Gravity Corer	Jan 12/78	15	190	30.225
	Feb 6/79	15	215	30.631
Divers	Feb 29/79	56.2	7	-----
		57.2	9	-----
		59.0	9	-----
	Jan 22/80	56.2	15	27.143
		57.2	13	25.439
		59.0	13	23.619
	Jan 25/80	60.5	18	21.288
		62.2	17	11.579
		62.5	16	13.101
		67.0	13	0.0

APPENDIX B Data Summary of Aqueous Samples

APPENDIX B.1 Dissolved Constituents

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk (meq/l)	Dis Mn (ppb)
78-01	1.0	1	5.98	27.582	6.78	7.73	2.03	2.60
78-01	1.0	5	6.28	27.812	6.68	7.73	2.09	1.43
78-01	1.0	10	7.23	28.659	6.07	7.71	2.15	0.82
78-01	1.0	25	8.04	29.242	5.39	7.72	2.10	0.49
78-01	1.0	50	8.22	29.585	4.86	7.69	2.12	0.47
78-01	1.0	100	8.95	30.233	3.89	7.64	2.21	0.41
78-01	1.0	200	9.23	30.910	3.52	7.64	2.20	1.07
78-01	1.0	300	9.02	31.098	3.30	7.60	2.26	1.78
78-01	1.0	390	N A ¹	31.098	3.00	7.60	2.22	6.81
78-01	2.0	1	5.83	27.405	6.85	7.76	2.04	2.53
78-01	2.0	5	5.87	27.405	6.85	7.77	2.00	N A
78-01	3.0	1	6.73	28.350	6.63	7.76	2.04	1.14
78-01	3.0	5	6.78	28.303	6.63	7.78	2.22	2.53
78-01	3.0	10	6.73	28.309	6.60	7.78	2.05	1.21
78-01	3.0	25	7.73	28.804	5.86	7.73	2.06	0.48
78-01	3.0	50	8.54	29.744	5.01	7.68	2.11	0.39
78-01	3.0	100	8.72	30.321	4.78	7.69	2.13	0.64
78-01	3.0	200	9.19	30.910	3.47	7.62	2.17	0.52
78-01	3.0	300	9.25	31.107	3.48	7.62	2.19	1.50
78-01	3.0	392	N A	N A	N A	N A	N A	7.91
78-01	4.0	1	5.73	26.597	7.01	7.76	1.96	4.08
78-01	4.0	5	5.65	26.615	7.08	7.77	1.96	N A
78-01	5.0	1	5.57	26.618	7.04	7.76	1.96	4.12
78-01	5.0	5	5.73	26.666	7.00	7.77	1.96	N A
78-01	6.0	1	6.16	27.588	6.59	7.74	2.00	2.25
78-01	6.0	5	6.40	27.766	6.44	7.77	2.00	N A
78-01	7.0	1	7.34	28.229	5.99	7.75	2.03	2.02
78-01	7.0	5	7.34	28.607	5.96	7.74	2.05	N A
78-01	8.0	1	7.41	28.243	6.06	7.69	2.03	2.65
78-01	8.0	5	7.61	28.528	5.88	7.67	2.04	N A
78-01	9.0	1	5.50	26.731	6.99	7.77	1.97	3.12
78-01	9.0	5	5.65	26.831	6.93	7.78	1.97	N A
78-01	10.0	1	4.91	26.351	7.22	7.77	1.93	3.57
78-01	10.0	5	4.93	26.344	7.23	7.78	1.94	N A
78-01	11.0	1	5.01	26.429	7.20	7.74	1.94	3.34
78-01	11.0	5	5.05	26.339	7.26	7.78	2.03	N A
78-01	12.0	1	5.41	26.593	7.01	7.74	1.95	3.22
78-01	12.0	5	5.45	26.596	7.01	7.75	1.95	N A
78-01	13.0	1	5.67	26.694	6.99	7.76	1.97	3.47
78-01	13.0	5	5.71	26.738	7.00	7.74	1.95	N A
78-01	14.0	1	5.72	21.857	6.80	7.70	1.84	9.29
78-01	14.0	5	7.36	28.361	6.15	7.74	2.02	N A

(1) N A = No Analysis

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-01	15.0	1	6.37	26.014	6.63	7.72	1.99	8.63
78-01	15.0	5	6.77	27.165	6.36	7.76	2.04	7.55
78-01	15.0	10	7.45	28.308	6.00	7.73	2.13	1.96
78-01	15.0	25	7.62	29.636	5.70	7.75	2.11	1.56
78-01	15.0	50	7.66	29.886	5.55	7.75	2.10	1.04
78-01	15.0	100	7.51	30.051	5.74	7.78	2.31	1.84
78-01	15.0	150	7.69	30.138	5.59	7.77	2.18	1.38
78-01	15.0	188	N A	30.225	5.23	7.76	2.14	2.44
78-01	16.0	1	5.49	25.630	7.02	7.76	1.93	5.52
78-01	16.0	5	5.68	26.467	6.98	7.74	1.98	N A
78-01	17.0	1	5.44	26.553	7.04	7.76	1.97	3.80
78-01	17.0	5	5.52	26.613	7.02	7.76	1.94	N A
78-01	18.0	1	5.96	27.024	6.63	7.78	1.97	3.26
78-01	18.0	5	6.12	26.993	6.63	7.77	1.97	N A
78-01	19.0	1	7.00	27.937	6.15	7.74	2.02	5.01
78-01	19.0	5	7.32	28.652	5.96	7.75	1.93	N A
78-01	20.0	1	5.83	25.382	7.00	7.71	1.93	6.76
78-01	20.0	5	6.22	26.736	6.74	7.73	2.00	4.85
78-01	21.0	1	6.18	26.497	6.73	7.74	1.77	5.51
78-01	21.0	5	6.28	26.620	6.68	7.73	1.98	4.66
78-01	22.0	1	7.39	29.706	5.90	7.73	2.10	2.03
78-01	22.0	5	7.41	29.658	5.90	7.73	2.18	4.43
78-01	23.0	1	7.41	29.555	5.89	7.74	2.10	1.99
78-01	23.0	5	7.48	29.619	5.83	7.73	2.14	1.77
78-01	24.0	1	7.25	29.213	6.01	7.74	2.09	2.54
78-01	24.0	5	7.37	29.309	5.94	7.74	2.09	2.22
78-01	25.0	1	6.94	28.102	6.16	7.72	2.07	2.81
78-01	25.0	5	6.97	28.059	6.25	7.74	2.03	2.64
78-01	25.0	10	7.57	28.923	5.76	7.69	2.08	1.39
78-01	25.0	25	7.60	29.604	5.70	7.70	2.10	2.81
78-01	25.0	50	7.57	29.793	5.70	7.71	2.15	1.72
78-01	25.0	100	7.54	29.899	5.75	7.72	2.23	1.76
78-01	25.0	150	7.63	30.039	5.70	7.73	2.14	1.37
78-01	25.0	210	N A	30.143	5.52	7.73	2.13	1.55
78-01	26.0	1	7.53	29.822	5.79	7.73	2.11	N A
78-01	26.0	5	7.57	29.823	5.77	7.74	2.12	1.55
78-01	51.0	1	N A	20.702	N A	7.69	1.74	4.16
78-01	51.0	100	N A	29.925	N A	7.72	2.13	3.07
78-01	52.0	1	N A	23.734	N A	7.69	1.84	8.82
78-01	52.0	50	N A	29.825	N A	7.70	2.12	4.87

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-04	15.0	1	8.66	26.837	6.81	7.71	N A	4.12
78-04	15.0	5	8.59	27.356	6.52	7.77	1.99	N A
78-04	15.0	10	8.57	27.379	6.73	7.72	2.02	1.29
78-04	15.0	20	8.01	28.424	6.90	N A	N A	N A
78-04	15.0	25	7.87	29.085	5.68	7.60	2.08	1.33
78-04	15.0	30	7.84	29.551	5.74	N A	N A	N A
78-04	15.0	50	7.86	29.789	5.60	7.63	2.12	0.37
78-04	15.0	75	7.93	29.951	5.79	N A	N A	N A
78-04	15.0	100	7.96	30.019	5.73	7.71	2.13	0.87
78-04	15.0	150	8.09	30.187	5.45	7.69	2.13	1.01
78-04	15.0	177	N A	30.296	5.55	7.68	2.16	1.43
78-04	53.0	1	7.44	12.634	7.24	7.58	1.52	13.4
78-04	53.0	12	7.41	29.712	5.42	7.63	2.10	4.49
78-04	54.0	1	6.74	7.649	8.00	7.64	1.37	14.5
78-04	54.0	16	6.80	28.469	5.72	7.69	2.06	2.77
78-04	55.0	1	6.81	5.970	8.22	7.60	1.37	14.8
78-04	55.0	20	6.78	28.392	5.70	7.60	2.07	2.52
78-04	56.0	1	6.54	5.364	8.27	7.58	1.32	17.1
78-04	56.0	13	6.53	27.495	5.84	7.62	2.01	3.28
78-04	57.0	1	6.54	4.028	8.43	7.59	1.20	17.6
78-04	57.0	17	6.33	24.622	6.18	7.64	1.92	6.91
78-04	58.0	1	6.59	2.226	8.62	7.60	1.24	16.6
78-04	58.0	17	6.50	23.425	6.18	7.65	1.88	7.68
78-04	59.0	1	6.36	2.055	8.60	7.60	1.26	16.2
78-04	59.0	6	6.33	21.378	6.43	7.60	1.82	10.2
78-04	61.0	1	6.09	0.039	8.88	7.65	1.22	11.4
78-04	61.0	12	6.14	14.444	7.22	7.56	1.59	14.7
78-04	63.0	1	6.05	0.0	8.90	7.70	1.31	11.1
78-04	63.0	12	6.11	0.0	8.91	7.66	1.20	13.0
78-04	65.0	1	6.08	0.0	8.91	7.68	1.18	9.97
78-04	65.0	16	6.11	0.0	8.92	7.73	1.19	11.7

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-07	1.0	1	13.26	26.165	7.96	8.32	1.91	2.88
78-07	1.0	5	12.21	26.912	9.16	8.36	1.95	2.26
78-07	1.0	10	10.80	28.590	6.70	7.96	2.00	1.04
78-07	1.0	25	9.50	29.445	5.32	7.70	2.06	0.45
78-07	1.0	50	8.87	29.717	4.59	7.58	2.03	0.25
78-07	1.0	100	8.44	29.979	4.05	7.51	N A	2.65
78-07	1.0	200	8.95	30.743	3.33	7.51	2.06	1.07
78-07	1.0	300	9.15	30.942	2.24	7.48	2.08	0.71
78-07	1.0	324	N A	30.966	2.63	7.48	2.24	5.70
78-07	2.0	1	13.37	26.015	7.71	8.30	1.90	3.40
78-07	2.0	5	12.94	26.176	7.80	8.28	1.87	3.36
78-07	3.0	1	12.60	25.918	9.17	8.39	1.85	7.84
78-07	3.0	5	12.12	26.810	9.38	8.31	1.95	6.54
78-07	3.0	10	10.47	28.627	6.98	7.97	1.99	6.54
78-07	3.0	25	8.85	29.450	5.06	7.64	2.06	1.61
78-07	3.0	50	8.33	29.743	4.55	7.56	2.00	1.02
78-07	3.0	100	8.35	30.072	4.73	7.62	2.01	0.34
78-07	3.0	200	8.79	30.622	4.16	7.60	2.11	1.30
78-07	3.0	300	9.00	30.872	3.15	7.51	2.11	1.80
78-07	3.0	420	N A	30.975	3.73	7.58	2.13	9.02
78-07	4.0	1	12.09	26.629	9.02	8.33	1.95	1.80
78-07	4.0	5	11.85	26.806	9.43	8.32	1.87	1.41
78-07	5.0	1	12.70	24.975	8.29	8.29	1.85	2.54
78-07	5.0	5	12.19	25.959	8.18	8.25	1.90	1.92
78-07	6.0	1	11.91	25.027	7.33	8.15	1.70	4.96
78-07	6.0	5	10.94	27.183	6.69	7.99	1.92	1.69
78-07	7.0	1	12.71	18.256	7.49	8.27	1.35	6.53
78-07	7.0	5	10.86	26.855	5.89	7.83	1.91	3.66
78-07	8.0	1	12.61	20.440	7.55	8.25	1.43	4.73
78-07	8.0	5	10.15	27.992	5.78	7.83	1.91	1.15
78-07	9.0	1	12.35	25.379	7.45	8.24	1.81	4.58
78-07	9.0	5	11.61	27.330	7.84	8.09	1.95	1.89
78-07	10.0	1	12.41	21.641	7.49	8.25	1.81	4.52
78-07	10.0	5	12.24	27.315	5.96	8.02	2.00	1.83
78-07	11.0	1	12.41	25.844	8.26	8.36	1.59	3.01
78-07	11.0	5	12.45	25.845	8.23	8.37	1.85	2.96
78-07	12.0	1	12.45	22.995	8.06	8.27	1.70	4.55
78-07	12.0	5	11.42	27.193	8.66	8.21	1.95	1.65
78-07	13.0	1	13.79	21.472	7.94	8.39	1.21	4.23
78-07	13.0	5	13.05	24.537	8.46	8.35	1.82	2.45
78-07	14.0	1	12.41	21.641	7.49	8.20	1.63	6.41
78-07	14.0	5	12.24	27.315	5.96	7.86	1.94	2.96
78-07	15.0	1	13.55	19.574	8.43	8.40	1.48	7.95
78-07	15.0	5	13.23	21.894	8.60	8.43	1.65	11.7
78-07	15.0	10	10.21	28.551	6.07	7.88	1.95	4.96
78-07	15.0	25	8.74	29.519	5.18	7.69	1.99	2.14
78-07	15.0	50	9.16	29.901	5.18	7.76	2.04	6.06
78-07	15.0	100	8.69	30.165	5.00	7.70	2.06	6.20
78-07	15.0	150	8.81	30.552	4.67	7.68	2.07	2.48
78-07	15.0	180	N A	30.643	4.22	7.65	2.07	8.57
78-07	16.0	1	12.96	22.082	8.70	8.39	1.69	5.35
78-07	16.0	5	13.03	22.170	8.66	8.40	1.69	5.35
78-07	17.0	1	12.91	20.224	8.79	8.42	1.63	7.03

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-07	17.0	5	11.54	24.321	8.03	8.19	1.81	5.73
78-07	18.0	1	12.87	21.065	8.24	8.39	1.63	6.44
78-07	18.0	5	12.75	21.086	8.14	8.39	1.63	6.59
78-07	19.0	1	11.33	23.394	6.43	8.05	1.65	6.50
78-07	19.0	5	9.96	28.619	5.84	7.86	1.95	4.55
78-07	20.0	1	12.17	21.808	7.99	8.19	1.69	6.21
78-07	20.0	5	12.02	24.058	7.57	8.24	1.79	5.05
78-07	21.0	1	N A	21.491	7.94	8.35	1.69	6.50
78-07	21.0	5	N A	21.552	8.04	8.33	1.69	5.97
78-07	22.0	1	10.56	26.270	6.86	8.00	1.85	1.77
78-07	22.0	5	9.48	29.215	5.76	7.83	1.99	1.24
78-07	23.0	1	12.00	22.639	7.69	8.22	1.68	6.86
78-07	23.0	5	11.79	23.447	7.94	8.25	1.74	4.91
78-07	23.5	1	11.85	23.665	8.14	8.28	1.72	4.70
78-07	23.5	5	11.62	23.891	8.10	8.28	1.74	4.70
78-07	24.0	1	11.21	29.219	7.44	8.15	2.00	2.96
78-07	24.0	5	11.21	29.222	7.49	8.16	2.07	2.96
78-07	25.0	1	10.19	28.132	6.12	7.92	1.95	2.43
78-07	25.0	5	10.07	29.274	6.12	7.91	1.96	2.26
78-07	25.0	10	10.02	29.473	5.99	7.89	2.00	1.69
78-07	25.0	25	9.78	29.697	5.84	7.88	2.00	1.55
78-07	25.0	50	9.73	29.854	5.77	7.86	2.02	1.41
78-07	25.0	100	9.36	30.306	5.31	7.81	2.06	0.99
78-07	25.0	150	9.40	30.428	5.34	7.81	2.06	1.02
78-07	25.0	218	N A	30.616	5.18	7.79	2.07	2.09
78-07	26.0	1	9.49	30.243	5.44	7.82	2.07	1.18
78-07	26.0	5	9.49	30.251	5.45	7.82	2.04	1.36
78-07	53.0	1	N A	0.364	7.71	7.95	0.82	5.06
78-07	54.0	1	N A	0.271	7.78	7.96	0.83	2.81
78-07	55.0	1	N A	0.0	7.79	8.01	0.85	3.24
78-07	56.0	1	N A	0.0	7.80	8.01	0.81	3.39

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-10	15.0	1	16.17	14.626	6.82	N A	N A	4.40
78-10	15.0	5	16.22	23.399	6.95	N A	1.85	3.36
78-10	15.0	10	14.94	26.711	6.97	N A	1.97	0.98
78-10	15.0	25	10.47	29.205	5.28	N A	2.08	0.93
78-10	15.0	50	9.45	29.837	4.65	N A	2.10	0.49
78-10	15.0	100	9.21	30.217	4.51	N A	2.12	0.52
78-10	15.0	150	9.05	30.512	4.27	N A	2.14	0.55
78-10	15.0	188	N A	30.652	4.22	N A	2.15	5.83
78-10	70.0	0	N A	0.0	N A	N A	1.19	4.28

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-11	58.0	1	N A	0.0	N A	N A	0.96	1.97
78-11	58.0	9	N A	0.0	N A	N A	0.96	2.03
78-11	55.5	1	N A	0.0	N A	N A	1.00	2.93
78-11	55.5	9	N A	19.580	N A	N A	1.65	13.3
78-11	56.2	1	N A	0.0	N A	N A	0.93	2.78
78-11	56.2	9	N A	18.463	N A	N A	1.61	11.0
78-11	56.4	9	N A	4.887	N A	N A	1.01	5.96
78-11	56.5	9	N A	10.016	N A	N A	1.27	10.3
78-11	56.6	9	N A	2.380	N A	N A	0.89	6.71

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-12	15.0	0	19.1	19.917	N A	N A	N A	N A
78-12	15.0	1	19.12	19.685	6.80	8.39	1.69	3.36
78-12	15.0	5	16.76	24.026	6.79	8.24	1.85	2.60
78-12	15.0	10	13.67	26.749	6.06	8.05	1.99	1.91
78-12	15.0	20	11.46	29.104	4.82	N A	N A	N A
78-12	15.0	25	10.41	29.391	4.58	7.68	2.09	0.67
78-12	15.0	30	10.09	29.509	4.34	N A	N A	N A
78-12	15.0	50	9.37	29.668	4.20	7.58	2.09	0.17
78-12	15.0	75	9.84	30.057	4.14	7.65	2.11	0.23
78-12	15.0	100	10.16	30.364	4.10	7.68	2.14	2.81
78-12	15.0	150	9.70	30.683	4.10	7.69	2.14	0.81
78-12	15.0	194	N A	30.622	4.01	7.69	2.15	3.44

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-13	1.0	5	13.19	26.726	6.55	N A	N A	0.39
78-13	1.0	10	11.92	28.225	5.06	N A	N A	0.28
78-13	1.0	25	10.94	28.807	4.32	N A	N A	0.36
78-13	1.0	50	9.91	29.450	3.70	N A	N A	0.33
78-13	1.0	100	9.50	30.231	3.55	N A	N A	0.0
78-13	1.0	200	9.00	N A	3.18	N A	N A	0.53
78-13	1.0	300	9.03	30.932	3.13	N A	N A	0.0
78-13	1.0	351	N A	30.208	3.79	N A	N A	3.78

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-16	70.0	0	12.3	0.0	N A	N A	1.17	18.8
78-16	70.0	0	12.3	0.0	N A	7.93	1.08	14.0
78-16	70.0	0	12.3	0.0	N A	7.86	1.07	8.63
78-16	70.0	0	12.3	0.0	N A	7.85	1.06	7.89
78-16	70.0	0	11.7	0.0	N A	7.94	1.06	6.03
78-16	70.0	0	11.5	0.0	N A	N A	1.05	4.65
78-16	15.0	1	12.71	24.416	6.63	8.00	1.84	4.64
78-16	15.0	5	12.48	26.739	5.91	7.87	N A	0.67
78-16	15.0	10	11.72	29.271	4.96	7.75	2.00	0.70
78-16	15.0	25	10.40	N A	3.99	7.60	2.05	0.34
78-16	15.0	50	9.88	N A	3.64	7.52	2.09	0.25
78-16	15.0	75	10.16	29.937	3.82	7.61	2.11	0.87
78-16	15.0	100	10.11	30.143	3.89	7.60	2.12	0.83
78-16	15.0	150	9.71	30.752	3.65	7.59	2.13	1.56
78-16	15.0	196	N A	30.968	3.49	7.56	2.16	3.62
78-16	15.0	1	12.86	22.594	6.91	N A	N A	N A
78-16	15.0	5	12.69	25.527	6.69	N A	N A	N A
78-16	15.0	10	11.16	28.408	4.49	N A	N A	N A
78-16	15.0	25	10.12	29.387	3.80	N A	N A	N A
78-16	15.0	50	10.15	29.769	3.87	N A	N A	N A
78-16	15.0	75	10.14	29.982	3.96	N A	N A	N A
78-16	15.0	100	9.93	30.232	3.95	N A	N A	N A
78-16	15.0	150	9.73	30.706	3.60	N A	N A	N A
78-16	15.0	1	12.88	24.160	6.94	8.06	1.82	2.15
78-16	15.0	5	12.79	25.337	6.88	8.05	1.86	1.06
78-16	15.0	10	11.09	28.297	4.47	7.67	1.93	0.44
78-16	15.0	25	N A	29.390	3.78	7.56	2.00	0.33
78-16	15.0	50	N A	29.806	3.80	7.60	2.04	0.61
78-16	15.0	75	N A	30.037	3.96	7.62	2.04	1.44
78-16	15.0	100	N A	30.285	3.86	7.62	2.06	1.03
78-16	15.0	150	N A	30.747	3.60	7.58	2.09	0.69
78-16	15.0	187	N A	30.963	3.46	7.57	2.11	4.94
78-16	15.0	188	N A	N A	N A	N A	N A	4.86
78-16	50.0	1	12.5	21.348	6.71	7.99	1.71	3.33
78-16	50.0	1	12.9	25.236	6.89	8.03	1.87	0.67
78-16	50.0	141	10.0	30.564	3.74	7.59	2.15	2.29
78-16	53.0	1	11.8	11.329	6.79	7.88	1.25	5.50
78-16	53.0	11	10.2	29.591	4.00	7.65	2.09	2.49
78-16	53.0	1	11.7	7.063	7.00	7.79	1.10	6.03
78-16	53.0	11	10.8	29.645	4.03	7.62	2.06	2.42
78-16	53.0	1	11.6	6.171	7.22	7.80	0.92	6.01
78-16	53.3	1	11.6	16.255	6.52	7.91	1.47	4.50
78-16	53.6	1	11.8	11.677	6.81	7.86	1.24	4.88
78-16	53.6	9	10.3	28.951	4.31	7.62	2.03	2.02
78-16	54.0	1	11.9	9.887	6.77	7.80	1.21	5.30
78-16	54.3	1	11.9	11.572	6.68	7.80	1.18	5.57
78-16	54.3	10	10.3	29.236	4.19	7.60	2.07	2.33
78-16	54.3	1	12.0	8.852	6.99	7.87	1.05	5.99
78-16	54.3	1	12.0	7.054	7.12	7.86	1.09	6.87
78-16	55.0	1	11.3	1.411	7.49	7.74	1.08	5.65
78-16	55.3	1	11.7	1.535	7.46	7.72	1.09	6.50
78-16	55.5	1	11.3	0.703	7.58	7.79	1.07	5.52
78-16	56.0	1	11.3	0.628	7.58	7.75	1.07	4.77

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-16	57.0	12	11.3	24.986	5.18	7.74	1.89	4.59
78-16	57.0	13	11.3	24.382	5.26	7.75	1.84	N A
78-16	57.5	13	11.3	20.762	5.60	7.79	1.66	5.48
78-16	56.3	11	11.3	26.969	4.85	7.72	1.96	3.62
78-16	56.3	1	11.3	0.570	7.56	7.78	N A	10.6
78-16	56.3	11	11.3	22.925	5.23	7.77	1.77	12.6
78-16	56.3	15	11.3	20.677	5.40	7.78	1.63	8.62
78-16	56.3	9	11.3	11.859	6.21	7.79	1.26	8.55
78-16	56.3	8	11.3	8.303	6.48	7.80	1.24	8.80
78-16	56.3	9	11.3	11.993	6.08	7.81	1.37	8.29
78-16	56.3	8	11.3	11.023	6.30	7.80	1.27	9.77
78-16	56.3	7	11.3	12.114	6.33	7.80	1.32	8.59
78-16	56.3	7	11.3	12.558	6.19	7.81	1.34	8.75
78-16	56.3	7	11.3	10.873	6.49	7.80	1.30	8.42
78-16	56.3	7	11.3	9.810	6.50	7.80	1.22	8.27
78-16	56.3	8	11.3	9.531	6.60	7.78	1.22	9.42
78-16	56.3	8	11.3	8.658	6.66	7.78	1.19	9.51
78-16	56.3	9	11.3	26.095	4.84	7.75	1.91	4.95
78-16	56.3	9	11.3	26.740	4.86	7.75	1.93	4.28
78-16	56.3	9	11.3	26.922	4.71	7.75	1.93	4.28
78-16	56.3	1	11.3	0.874	N A	N A	N A	4.97
78-16	56.3	1	11.3	0.874	7.57	7.83	1.07	4.83
78-16	56.3	9	11.6	26.530	5.41	7.75	1.87	2.67
78-16	58.3	15	11.2	23.394	5.46	7.80	1.76	6.03
78-16	58.3	1	12.0	0.039	7.56	7.82	0.85	6.49
78-16	58.3	13	11.2	22.820	5.51	7.79	1.71	6.67
78-16	58.3	13	11.2	22.901	5.51	7.79	1.72	7.00
78-16	58.3	13	11.2	22.858	5.51	7.82	1.72	7.61
78-16	58.3	14	11.2	22.813	5.54	7.82	1.67	6.78
78-16	58.3	13	11.2	21.706	5.57	7.80	1.72	7.58
78-16	58.5	11	11.2	4.171	7.12	7.77	0.93	7.83
78-16	58.5	1	11.2	0.003	7.66	7.86	0.92	N A
78-16	59.0	16	11.2	22.139	5.53	7.79	1.69	N A
78-16	59.0	1	11.2	0.0	7.66	7.84	0.89	5.47
78-16	60.0	16	11.2	0.786	7.52	7.78	0.88	6.40
78-16	60.0	1	11.2	0.0	7.72	7.88	0.86	4.54
78-16	61.0	12	11.2	0.0	7.72	7.80	0.86	3.98
78-16	61.0	1	11.2	0.0	7.71	7.82	0.86	3.98
78-16	62.0	17	11.2	0.0	7.66	7.80	0.85	4.08
78-16	62.0	1	11.2	0.0	7.67	7.79	0.85	4.08
78-16	63.0	13	11.2	0.0	7.73	7.84	0.87	4.65
78-16	63.0	1	11.2	0.0	7.70	7.81	0.87	4.54
78-16	56.0	1	11.2	2.282	7.41	7.74	0.92	7.17
78-16	55.0	1	11.2	6.379	7.26	7.87	0.98	7.11
78-16	54.0	1	11.2	14.295	6.95	7.97	1.36	6.92
78-16	53.0	1	11.2	12.697	6.90	7.94	1.24	7.64
78-16	51.0	1	11.2	15.095	6.73	7.95	1.35	5.44

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
78-20	15.0	1	8.64	28.885	5.67	7.71	N A	0.83
78-20	15.0	5	8.66	28.878	5.58	7.71	N A	0.93
78-20	15.0	10	8.62	28.831	5.47	7.70	N A	1.07
78-20	15.0	25	9.01	30.034	4.30	7.66	N A	N A
78-20	15.0	50	9.07	30.180	4.18	7.67	N A	0.83
78-20	15.0	75	9.15	30.346	4.18	7.69	N A	0.69
78-20	15.0	100	8.91	30.418	4.43	7.68	N A	0.69
78-20	15.0	150	8.42	30.467	4.61	7.70	N A	1.16
78-20	15.0	186	N A	30.560	4.62	7.70	N A	2.54

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-01	1.0	1	7.15	29.636	6.21	7.69	2.05	0.67
79-01	1.0	5	7.14	29.614	6.19	7.68	2.05	0.64
79-01	1.0	10	7.18	29.572	6.14	7.68	2.05	0.56
79-01	1.0	25	7.28	29.655	6.11	7.69	2.05	0.45
79-01	1.0	50	7.49	29.733	5.98	7.63	2.05	0.49
79-01	1.0	75	8.45	29.976	4.71	7.63	2.07	0.45
79-01	1.0	100	9.32	30.571	3.72	7.60	2.10	0.26
79-01	1.0	150	9.18	30.841	3.53	7.63	2.12	0.60
79-01	1.0	200	9.16	31.015	3.37	7.60	2.13	0.0
79-01	1.0	300	9.29	31.144	3.13	7.58	2.13	1.01
79-01	1.0	362	N A	31.180	3.27	7.60	2.15	4.79
79-01	2.0	1	7.28	29.687	6.19	7.69	2.05	0.64
79-01	3.0	1	7.32	29.623	6.13	7.70	2.05	0.45
79-01	3.0	5	7.32	29.632	6.07	7.69	2.05	0.67
79-01	3.0	10	7.36	29.613	6.06	7.48	2.06	0.45
79-01	3.0	25	7.33	29.601	6.06	7.70	2.05	0.45
79-01	3.0	50	7.34	29.655	6.08	7.68	2.06	0.45
79-01	3.0	75	8.73	30.078	4.30	7.64	2.08	0.23
79-01	3.0	100	8.86	30.530	4.13	7.63	2.11	0.34
79-01	3.0	200	8.16	30.769	4.68	7.65	2.12	1.57
79-01	3.0	300	8.95	31.029	3.63	7.63	2.13	1.61
79-01	3.0	350	9.05	31.084	3.52	7.62	2.14	1.29
79-01	3.0	422	N A	31.110	3.71	7.65	2.14	8.14
79-01	4.0	1	6.53	29.213	6.14	7.74	2.04	1.29
79-01	5.0	1	6.46	29.303	6.26	7.72	2.04	0.82
79-01	6.0	1	6.49	29.294	6.21	7.73	2.03	0.71
79-01	7.0	1	6.27	29.003	N A	7.73	1.99	1.01
79-01	8.0	1	5.98	28.527	6.04	7.68	2.02	2.11
79-01	9.0	1	7.17	29.355	5.95	7.75	2.05	0.23
79-01	10.0	1	7.00	29.414	6.16	7.75	2.05	0.0
79-01	11.0	1	7.31	29.508	5.96	7.75	2.02	0.67
79-01	12.0	1	6.05	28.788	6.66	7.72	2.02	1.79
79-01	13.0	1	5.75	28.565	6.72	7.70	2.01	2.11
79-01	14.0	1	6.15	29.150	6.45	7.68	2.03	1.43
79-01	15.0	1	5.60	28.368	6.53	7.68	1.99	3.37
79-01	15.0	5	5.75	28.694	6.32	7.69	2.02	3.05
79-01	15.0	10	5.95	28.844	6.14	7.66	2.01	3.19
79-01	15.0	25	7.07	30.092	5.68	7.67	2.08	2.08
79-01	15.0	50	7.33	30.326	5.57	7.67	2.08	1.36
79-01	15.0	75	7.27	30.346	5.65	7.70	N A	1.72
79-01	15.0	100	7.23	30.348	5.58	7.67	2.11	1.43
79-01	15.0	150	7.33	30.389	5.54	7.66	2.11	1.51
79-01	15.0	200	N A	30.447	5.40	7.66	2.11	1.90
79-01	16.0	1	5.93	28.745	6.70	7.72	2.03	1.90
79-01	17.0	1	5.78	28.599	6.75	7.71	2.02	2.29
79-01	18.0	1	5.2	27.989	6.81	7.69	2.00	3.15
79-01	19.0	1	5.9	28.750	6.20	7.67	2.05	4.26
79-01	20.0	1	5.7	28.745	6.54	7.68	2.04	3.01
79-01	21.0	1	6.5	29.050	6.31	7.71	2.04	1.68
79-01	22.0	1	7.1	30.230	5.74	8.06	2.12	1.36
79-01	23.0	1	7.1	29.591	5.74	7.68	2.08	2.19
79-01	24.0	1	7.0	30.316	5.68	8.10	2.11	1.36
79-01	25.0	1	7.3	29.963	5.16	8.14	2.08	1.18

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-01	26.0	1	6.9	30.315	5.87	8.15	2.11	1.36
79-01	15.0	1	5.1	26.998	6.37	7.92	1.99	7.53
79-01	50.0	1	5.5	27.962	6.32	7.97	2.04	6.70
79-01	50.0	1	5.5	27.873	6.32	7.93	2.02	6.45
79-01	51.0	1	6.1	29.407	5.08	7.94	2.07	3.23
79-01	51.0	1	6.2	28.659	6.10	7.93	2.05	5.27
79-01	52.0	1	6.3	29.200	N A	7.96	2.07	3.60
79-01	52.0	1	6.3	28.991	6.10	7.95	2.06	4.38
79-01	53.0	1	5.9	28.346	6.19	7.94	2.03	5.23
79-01	53.0	1	5.9	28.247	6.20	7.94	2.02	5.15
79-01	53.3	1	5.8	28.471	6.13	7.95	2.04	4.99
79-01	53.3	1	5.9	28.507	6.13	7.98	2.04	4.38
79-01	53.6	1	5.8	28.386	6.05	8.00	2.04	5.43
79-01	53.6	1	6.0	28.454	6.21	7.99	2.05	5.19
79-01	54.0	1	6.40	29.024	4.61	7.98	2.06	4.22
79-01	54.0	1	6.22	28.899	6.02	7.95	2.05	4.74
79-01	54.3	1	5.21	28.382	6.41	7.93	2.03	5.52
79-01	54.3	1	5.30	28.506	5.05	7.92	2.03	5.19
79-01	55.0	1	2.76	16.490	7.78	7.89	1.59	16.9
79-01	55.0	1	2.73	15.859	7.86	7.88	1.57	16.9
79-01	55.3	1	2.07	14.010	8.04	7.87	1.51	20.6
79-01	55.3	14	N A	28.280	5.73	N A	2.02	9.57
79-01	55.3	1	2.30	13.945	8.07	7.89	1.49	N A
79-01	55.5	1	1.35	12.820	8.17	7.87	1.46	19.3
79-01	55.5	1	1.90	10.971	8.43	7.82	1.38	20.6
79-01	56.0	1	2.38	14.593	7.93	7.87	1.52	17.7
79-01	56.0	10	N A	25.397	6.50	N A	1.93	8.84
79-01	56.0	1	2.40	15.677	7.78	7.89	1.57	17.4
79-01	57.0	1	1.75	10.018	8.49	7.85	1.34	18.6
79-01	57.0	9	N A	21.587	7.04	N A	1.79	10.9
79-01	57.5	1	1.50	8.804	8.68	7.83	1.30	23.9
79-01	58.0	1	1.30	8.111	8.76	7.82	1.25	21.9
79-01	58.3	1	1.36	8.141	8.72	7.80	1.26	20.6
79-01	58.5	1	0.92	5.834	9.07	7.76	1.19	21.5
79-01	61.0	1	0.91	1.193	9.78	7.79	1.11	16.5
79-01	63.0	0	0.2	0.155	N A	7.82	1.14	14.9
79-01	65.0	0	0.2	0.060	N A	7.84	1.15	15.3

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-02	15.0	1	5.81	27.835	6.87	N A	2.04	3.90
79-02	15.0	5	5.83	28.095	6.76	N A	2.04	2.89
79-02	15.0	10	6.06	28.804	6.64	N A	2.07	2.57
79-02	15.0	25	6.73	29.869	5.92	N A	2.10	2.07
79-02	15.0	50	7.40	30.432	5.32	N A	2.14	1.01
79-02	15.0	75	N A	30.607	5.57	N A	2.14	0.51
79-02	15.0	100	6.76	30.615	5.79	N A	2.14	2.34
79-02	15.0	150	6.83	30.667	5.73	N A	2.14	0.87
79-02	15.0	215	N A	30.631	5.75	N A	2.14	2.30
79-02	25.0	1	7.05	30.071	5.61	N A	2.11	1.10
79-02	25.0	5	7.18	30.180	5.61	N A	2.11	0.87
79-02	25.0	10	7.36	30.262	5.39	N A	2.11	0.46
79-02	25.0	25	7.45	30.314	5.36	N A	2.11	0.46
79-02	25.0	50	7.22	30.401	5.49	N A	2.11	0.46
79-02	25.0	75	6.92	30.448	5.82	N A	2.12	0.23
79-02	25.0	100	6.88	30.560	5.78	N A	2.12	0.14
79-02	25.0	150	6.88	30.654	5.73	N A	2.12	0.14
79-02	25.0	188	N A	30.834	5.65	N A	2.13	0.09

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-05	15.0	1	7.25	20.066	7.32	7.73	N A	11.0
79-05	15.0	5	7.45	28.723	7.08	7.83	N A	2.35
79-05	15.0	9	7.32	28.971	6.99	7.75	N A	1.84
79-05	15.0	14	7.09	29.373	5.78	7.76	N A	2.80
79-05	15.0	29	7.46	30.099	5.62	7.68	N A	1.74
79-05	15.0	54	7.37	30.300	5.45	7.72	N A	3.12
79-05	15.0	104	7.32	30.524	5.45	7.72	N A	1.94
79-05	15.0	154	7.22	30.608	5.09	7.70	N A	2.43
79-05	15.0	192	N A	30.705	5.01	7.67	N A	6.20

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-07	3.0	1	8.65	29.314	11.33	8.31	2.06	1.21
79-07	3.0	5	8.52	29.326	10.68	8.28	2.07	1.26
79-07	3.0	10	7.96	29.505	8.41	8.09	2.07	1.31
79-07	3.0	25	7.54	29.927	6.02	7.65	2.07	0.50
79-07	3.0	50	7.66	30.260	5.12	7.57	2.07	0.69
79-07	3.0	100	7.40	30.549	5.27	7.60	2.08	0.78
79-07	3.0	200	7.75	30.789	4.62	7.56	2.09	0.45
79-07	3.0	300	7.34	30.749	5.18	7.61	2.09	0.83
79-07	3.0	350	7.28	30.769	5.12	7.60	2.10	3.11
79-07	3.0	372	7.27	30.762	N A	N A	N A	4.34
79-07	3.0	382	7.29	30.745	N A	N A	N A	4.96
79-07	3.0	392	7.22	30.769	N A	N A	N A	8.43
79-07	3.0	396	7.24	30.769	N A	N A	N A	9.00
79-07	3.0	398	7.23	30.771	N A	N A	N A	8.76
79-07	3.0	400	7.26	30.770	N A	N A	N A	9.47
79-07	3.0	401	N A	30.769	5.11	7.59	2.10	8.95
79-07	15.0	1	7.48	10.599	8.72	7.93	1.27	10.7
79-07	15.0	5	8.20	29.161	8.89	8.23	2.06	1.19
79-07	15.0	10	8.08	29.295	8.44	8.10	2.06	0.97
79-07	15.0	25	7.59	29.906	6.13	7.71	2.07	0.31
79-07	15.0	50	7.49	30.130	5.72	7.65	2.09	0.36
79-07	15.0	75	7.60	30.265	5.92	7.70	2.10	0.74
79-07	15.0	100	7.58	30.281	5.93	7.69	2.10	0.78
79-07	15.0	150	7.60	30.355	5.84	7.69	2.10	1.59
79-07	15.0	156	7.55	30.374	N A	N A	N A	3.73
79-07	15.0	166	7.49	30.493	N A	N A	N A	4.06
79-07	15.0	176	7.34	30.618	N A	N A	N A	4.91
79-07	15.0	180	7.34	30.648	N A	N A	N A	6.43
79-07	15.0	182	7.33	30.671	N A	N A	N A	5.72
79-07	15.0	184	7.36	30.692	N A	N A	N A	5.58
79-07	15.0	185	N A	30.716	4.90	7.60	2.11	6.96
79-07	56.3	0	5.3	2.676	8.76	7.63	1.01	10.6

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-12	1.0	1	14.00	28.534	7.08	8.38	N A	0.68
79-12	1.0	5	13.86	28.574	7.15	8.38	N A	0.72
79-12	1.0	10	12.23	29.058	6.99	8.29	N A	0.38
79-12	1.0	25	10.32	29.715	5.83	8.01	N A	0.55
79-12	1.0	50	8.97	30.061	4.90	7.83	N A	0.30
79-12	1.0	100	7.78	30.321	4.82	7.72	N A	0.30
79-12	1.0	200	7.54	30.723	4.78	7.72	N A	0.34
79-12	1.0	300	7.50	30.791	4.57	7.69	N A	1.44
79-12	1.0	351	N A	30.791	4.47	7.69	N A	3.63
79-12	2.0	1	14.42	26.012	6.87	8.38	N A	2.32
79-12	3.0	1	14.00	24.789	6.89	8.36	N A	3.38
79-12	3.0	5	13.65	24.779	6.95	8.36	N A	1.10
79-12	3.0	10	10.89	28.506	6.69	8.31	N A	0.63
79-12	3.0	25	8.75	29.893	5.22	7.83	N A	0.17
79-12	3.0	50	8.03	30.138	4.83	7.75	N A	0.17
79-12	3.0	100	7.60	30.409	4.90	N A	N A	0.04
79-12	3.0	200	7.57	30.710	4.87	7.83	N A	0.25
79-12	3.0	300	7.44	30.749	4.84	7.71	N A	0.76
79-12	3.0	350	7.41	30.773	4.86	7.70	N A	1.77
79-12	3.0	420	N A	30.939	4.87	7.77	N A	18.4
79-12	4.0	1	13.91	26.509	6.99	8.32	N A	1.94
79-12	5.0	1	13.90	22.220	6.98	8.29	N A	5.70
79-12	6.0	1	14.74	16.695	7.54	8.31	N A	9.91
79-12	7.0	1	17.83	15.177	7.29	8.28	N A	10.7
79-12	8.0	1	13.64	18.445	7.08	8.19	N A	8.37
79-12	9.0	1	14.10	18.613	7.68	8.36	N A	8.62
79-12	10.0	1	13.91	19.090	7.19	8.28	N A	10.2
79-12	11.0	1	13.90	27.222	6.65	8.28	N A	1.18
79-12	12.0	1	15.60	17.705	8.99	8.62	N A	11.0
79-12	13.0	1	15.94	15.682	9.59	8.69	N A	13.4
79-12	14.0	1	15.82	17.500	9.29	8.64	N A	10.6
79-12	15.0	1	12.13	13.082	6.99	8.09	N A	9.66
79-12	15.0	5	13.17	24.234	7.09	8.25	N A	3.80
79-12	15.0	10	11.41	29.418	6.33	8.02	N A	0.46
79-12	15.0	25	8.60	30.048	5.03	7.73	N A	0.10
79-12	15.0	50	8.92	30.303	5.25	7.79	N A	0.30
79-12	15.0	75	8.99	30.382	5.28	7.80	N A	0.46
79-12	15.0	100	8.85	30.459	5.26	7.80	N A	0.50
79-12	15.0	150	8.83	30.749	5.06	7.79	N A	1.30
79-12	15.0	182	7.88	N A	N A	N A	N A	1.70
79-12	15.0	192	7.80	N A	N A	N A	N A	2.60
79-12	15.0	202	7.77	N A	N A	N A	N A	2.70
79-12	15.0	206	7.78	N A	N A	N A	N A	2.90
79-12	15.0	208	7.77	N A	N A	N A	N A	3.20
79-12	15.0	210	7.75	N A	N A	N A	N A	3.00
79-12	15.0	211	N A	30.714	4.92	7.64	N A	3.80
79-12	16.0	1	13.46	11.933	7.53	8.35	N A	15.9
79-12	17.0	1	14.34	20.316	8.79	8.60	N A	8.02
79-12	18.0	1	13.79	11.959	8.13	8.52	N A	12.1
79-12	19.0	1	11.45	18.447	6.54	8.07	N A	7.90
79-12	20.0	1	12.98	17.901	7.12	8.23	N A	10.0
79-12	21.0	1	13.54	18.249	7.68	8.36	N A	8.97
79-12	22.0	1	11.44	26.491	6.58	8.03	N A	3.13

Cruise	Stn	Depth (m)	Temp (°C)	Salinity (ppt)	Oxygen (ml/l)	pH	Alk meq/l	Dis Mn (ppb)
79-12	23.0	1	12.23	25.472	6.64	8.08	N A	3.87
79-12	24.0	1	10.48	29.916	6.10	7.96	N A	2.22
79-12	25.0	1	12.31	22.618	7.12	8.15	N A	5.83
79-12	25.0	5	10.50	28.315	6.28	7.97	N A	2.62
79-12	25.0	10	10.04	29.151	5.99	7.93	N A	2.41
79-12	25.0	25	9.94	29.530	5.89	7.93	N A	1.94
79-12	25.0	50	9.34	30.375	5.42	7.84	N A	1.44
79-12	25.0	75	9.17	30.573	5.27	7.82	N A	1.23
79-12	25.0	100	9.17	30.577	5.28	7.82	N A	1.44
79-12	25.0	150	9.11	30.635	5.24	7.81	N A	1.36
79-12	25.0	229	N A	30.741	5.05	7.73	N A	1.89
79-12	26.0	1	11.11	25.377	6.59	8.02	N A	4.18
79-12	15.0	1	12.51	9.558	8.02	8.33	N A	10.5
79-12	15.0	1	12.79	11.747	7.79	8.30	N A	12.7
79-12	50.0	1	12.65	12.842	7.53	8.23	N A	13.9
79-12	51.0	1	12.10	9.085	7.64	8.19	N A	13.8
79-12	51.0	1	12.32	12.280	8.18	8.37	N A	14.4
79-12	51.0	1	15.23	16.544	8.79	8.58	N A	10.8
79-12	51.0	1	15.44	16.061	9.04	8.64	N A	10.6
79-12	52.0	1	11.30	7.481	7.79	8.18	N A	6.91
79-12	52.0	1	10.8	8.176	7.48	8.04	N A	6.13
79-12	52.0	1	10.4	3.154	7.84	7.97	N A	9.30
79-12	53.0	1	10.7	0.053	8.06	8.11	N A	16.1
79-12	53.0	1	10.6	0.563	7.89	8.00	N A	18.0
79-12	53.0	1	10.8	6.412	7.38	7.94	N A	25.6
79-12	53.0	1	11.0	0.054	7.99	8.10	N A	17.4
79-12	56.0	1	11.20	0.0	8.09	8.14	N A	6.63
79-12	59.0	1	6.50	0.0	8.29	8.06	N A	5.27
79-12	65.0	1	10.65	0.0	8.24	8.14	N A	N A
79-12	15.0	1	13.75	10.416	8.74	8.48	N A	12.1
79-12	15.0	1	10.86	10.267	8.59	8.41	N A	12.5
79-12	15.0	1	13.52	8.986	N A	N A	N A	N A
79-12	15.5	1	13.0	6.294	8.35	8.36	N A	9.55
79-12	15.0	100	9.01	30.590	N A	N A	N A	N A
79-12	50.0	1	12.90	11.400	8.52	8.43	N A	14.6
79-12	52.0	1	11.1	5.890	7.76	8.08	N A	5.97
79-12	53.0	1	11.3	0.0	8.25	8.15	N A	10.1
79-12	53.0	11	9.0	30.027	5.33	7.79	N A	6.26
79-12	53.3	13	N A	29.610	5.41	7.80	N A	6.13
79-12	53.6	13	N A	28.604	5.59	7.79	N A	10.7
79-12	54.0	14	9.3	28.143	5.64	7.78	N A	12.4
79-12	54.3	14	N A	27.887	5.61	7.79	N A	11.1
79-12	54.6	11	N A	14.013	6.83	7.85	N A	16.7
79-12	55.0	11	N A	0.0	8.24	8.15	N A	5.33
79-12	55.3	12	N A	17.801	6.50	7.86	N A	18.7
79-12	55.5	11	N A	0.0	8.24	8.16	N A	4.83
79-12	56.0	13	N A	0.0	8.25	8.15	N A	4.50
79-12	56.6	10	N A	0.0	8.28	8.17	N A	4.20
79-12	57.0	13	N A	0.0	8.28	8.15	N A	N A

APPENDIX B.2 Particulate Constituents

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
78-04	53.0	1	12.634	13.4	3.84	274	298	
78-04	53.0	12	29.712	4.49	3.38	199	292	
78-04	54.0	1	7.649	14.5	4.45	347	384	
78-04	54.0	16	28.469	2.77	3.13	158	256	
78-04	55.0	1	5.970	14.8	4.69	371	400	
78-04	55.0	20	28.392	2.52	3.51	202	303	
78-04	56.0	1	5.364	17.1	4.87	378	446	
78-04	56.0	13	27.495	3.28	5.24	318	436	
78-04	57.0	1	4.028	17.6	4.79	370	405	
78-04	57.0	17	24.622	6.91	14.5	979	1440	
78-04	58.0	1	2.226	16.6	5.18	380	424	
78-04	58.0	17	23.425	7.68	5.47	375	512	
78-04	59.0	1	2.055	16.2	5.15	412	446	
78-04	59.0	6	21.378	10.2	4.64	325	423	
78-04	61.0	1	0.039	11.4	6.76	710	557	
78-04	61.0	12	14.444	14.7	5.55	377	493	
78-04	63.0	1	0.0	11.1	9.41	558	679	
78-04	63.0	12	0.0	13.0	8.67	537	701	
78-04	65.0	1	0.0	9.97	10.2	606	789	
78-04	65.0	16	0.0	11.7	10.6	654	849	

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
78-11	58.0	1	0.0	1.97	53.4	2810	5050	
78-11	58.0	9	0.0	2.03	72.2	4190	6770	
78-11	55.5	1	0.0	2.93	47.9	2540	4430	
78-11	55.5	9	19.580	13.3	96.6	5780	9310	
78-11	56.2	1	0.0	2.78	45.9	2580	4490	
78-11	56.2	9	18.463	11.0	56.9	3160	5410	
78-11	56.4	9	4.887	5.96	100.0	5370	9100	
78-11	56.5	9	10.016	10.3	107.0	5640	9730	
78-11	56.6	9	2.380	6.71	103.1	6240	10260	

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
78-16	70.0	0	0.0	18.8	13.5	932	1270	
78-16	70.0	0	0.0	14.0	19.3	1134	1610	
78-16	70.0	0	0.0	8.63	15.5	921	1340	
78-16	70.0	0	0.0	7.89	13.6	772	1140	
78-16	70.0	0	0.0	6.03	12.4	650	961	
78-16	70.0	0	0.0	4.65	12.6	625	907	
78-16	15.0	1	24.416	4.64	3.00	130	223	2.29
78-16	15.0	5	26.739	0.67	1.70	45.4	73	
78-16	15.0	10	29.271	0.70	0.70	4.0	4	
78-16	15.0	25	N A	0.34	0.70	1.7	1	
78-16	15.0	50	N A	0.25	1.10	7.4	11	
78-16	15.0	75	29.937	0.87	1.00	25.7	42	
78-16	15.0	100	30.143	0.83	1.10	24.9	40	
78-16	15.0	150	30.752	1.56	1.40	31.5	57	
78-16	15.0	196	30.968	3.62	5.60	326	475	6.17
78-16	15.0	1	24.160	2.15	1.60	42.2	61	
78-16	15.0	5	25.337	1.06	1.10	9.8	20	
78-16	15.0	10	28.297	0.44	0.60	3.3	7	
78-16	15.0	25	29.390	0.33	0.80	3.3	3	
78-16	15.0	50	29.806	0.61	1.10	11.3	15	
78-16	15.0	75	30.037	1.44	1.30	37.3	60	
78-16	15.0	100	30.285	1.03	1.10	26.3	40	
78-16	15.0	150	30.747	0.69	1.50	25.0	27	
78-16	15.0	187	30.963	4.94	2.60	129	212	3.59
78-16	15.0	188	N A	4.86	3.20	160	274	
78-16	50.0	1	21.348	3.33	2.90	132	232	3.67
78-16	50.0	1	25.236	0.67	1.10	9.4	13	2.00
78-16	50.0	141	30.564	2.29	2.80	156	275	4.59
78-16	53.0	1	11.329	5.50	6.50	346	512	6.44
78-16	53.0	11	29.591	2.49	4.40	244	442	7.53
78-16	53.0	1	7.063	6.03	7.20	407	558	7.67
78-16	53.0	11	29.645	2.42	3.70	202	384	5.60
78-16	53.0	1	6.171	6.01	7.50	421	583	7.44
78-16	53.3	1	16.255	4.50	5.90	320	471	6.25
78-16	53.6	1	11.677	4.88	6.20	329	490	6.12
78-16	53.6	9	28.951	2.02	4.90	296	433	7.20
78-16	54.0	1	9.887	5.30	6.40	349	510	6.28
78-16	54.3	1	11.572	5.57	5.70	317	471	5.75
78-16	54.3	10	29.236	2.33	5.40	327	494	6.40
78-16	54.3	1	8.852	5.99	7.40	368	533	6.41
78-16	54.3	1	7.054	6.87	7.00	356	491	6.92
78-16	55.0	1	1.411	5.65	10.0	609	857	9.92
78-16	55.3	1	1.535	6.50	11.6	746	1050	12.71
78-16	55.5	1	0.703	5.52	11.8	684	996	12.24
78-16	56.0	1	0.628	4.77	12.1	703	914	13.71
78-16	57.0	12	24.986	4.59	13.1	905	1370	19.88
78-16	57.0	13	24.382	N A	11.7	780	1240	15.20
78-16	57.5	13	20.762	5.48	19.9	1320	1870	31.28
78-16	56.3	11	26.969	3.62	6.30	431	569	8.33
78-16	56.3	1	0.570	10.6	21.1	1870	2030	24.08
78-16	56.3	11	22.925	12.6	5.60	501	583	8.75
78-16	56.3	15	20.677	8.62	28.7	1750	2730	42.71

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
78-16	56.3	9	11.859	8.55	46.6	2870	4700	56.08
78-16	56.3	8	8.303	8.80	45.6	2930	5070	
78-16	56.3	9	11.993	8.29	45.5	2830	4680	62.86
78-16	56.3	8	11.023	9.77	45.9	2870	4560	62.82
78-16	56.3	7	12.114	8.59	33.7	2170	3300	47.00
78-16	56.3	7	12.558	8.75	30.4	1790	3240	40.12
78-16	56.3	7	10.873	8.42	26.6	1620	2750	35.32
78-16	56.3	7	9.810	8.27	24.1	1510	2420	30.24
78-16	56.3	8	9.531	9.42	28.0	1710	2920	35.48
78-16	56.3	8	8.658	9.51	34.0	2070	3440	43.67
78-16	56.3	9	26.095	4.95	49.0	3100	5230	64.16
78-16	56.3	9	26.740	4.28	37.8	2440	4220	51.32
78-16	56.3	9	26.922	4.28	39.7	2460	4350	56.36
78-16	56.3	1	0.874	5.61	18.3	1280	1780	20.16
78-16	56.3	1	0.874	4.97	16.9	1110	1770	
78-16	56.3	1	0.874	4.83	8.60	1160	1680	
78-16	56.3	9	26.530	2.67	4.50	236	380	5.60
78-16	58.3	15	23.394	6.03	11.8	798	1130	14.48
78-16	58.3	1	0.039	6.49	12.2	703	917	11.96
78-16	58.3	13	22.820	6.67	9.80	637	954	11.24
78-16	58.3	13	22.901	7.00	10.7	713	1090	14.24
78-16	58.3	13	22.858	7.61	9.40	630	1050	12.60
78-16	58.3	14	22.813	6.78	9.80	685	1120	14.12
78-16	58.3	13	21.706	7.58	8.80	598	981	12.64
78-16	58.5	11	4.171	7.83	10.3	582	735	11.25
78-16	58.5	1	0.003	N A	13.1	698	1080	12.49
78-16	59.0	16	22.139	N A	6.90	399	592	7.71
78-16	59.0	1	0.0	5.47	11.5	594	828	11.12
78-16	60.0	16	0.786	6.40	14.9	842	1120	16.20
78-16	60.0	1	0.0	4.54	14.7	789	1160	14.69
78-16	61.0	12	0.0	3.98	16.6	911	1320	18.32
78-16	61.0	1	0.0	3.98	16.1	902	1290	14.04
78-16	62.0	17	0.0	4.08	14.8	798	1170	15.84
78-16	62.0	1	0.0	4.08	11.9	636	943	12.96
78-16	63.0	13	0.0	4.65	14.7	812	1190	14.75
78-16	63.0	1	0.0	4.54	14.1	711	1100	13.00
78-16	56.0	1	2.282	7.17	11.4	734	1010	11.80
78-16	55.0	1	6.379	7.11	10.5	679	980	11.43
78-16	54.0	1	14.295	6.92	4.40	337	495	5.76
78-16	53.0	1	12.697	N A	N A	N A	N A	6.68
78-16	51.0	1	15.095	5.44	2.70	128	215	5.56

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
79-01	15.0	1	26.998	7.53	1.60	124	182	
79-01	50.0	1	27.962	6.70	1.50	111	168	
79-01	50.0	1	27.873	6.45	1.60	124	192	
79-01	51.0	1	29.407	3.23	0.90	60.1	109	
79-01	51.0	1	28.659	5.27	1.20	96.5	142	
79-01	52.0	1	29.200	3.60	1.00	75.4	112	
79-01	52.0	1	28.991	4.38	1.20	87.8	141	
79-01	53.0	1	28.346	5.23	1.20	93.8	147	
79-01	53.0	1	28.247	5.15	1.10	89.6	142	
79-01	53.3	1	28.471	4.99	1.30	98.0	153	
79-01	53.3	1	28.507	4.38	1.60	114	161	
79-01	53.6	1	28.386	5.43	1.70	101	153	
79-01	53.6	1	28.454	5.19	1.50	97.2	158	
79-01	54.0	1	29.024	4.22	1.50	111	181	
79-01	54.0	1	28.899	4.74	1.10	97.1	153	
79-01	54.3	1	28.382	5.52	1.10	96.3	145	
79-01	54.3	1	28.506	5.19	1.10	96.3	148	
79-01	55.0	1	16.490	16.9	5.40	295	549	
79-01	55.0	1	15.859	16.9	5.50	355	526	
79-01	55.3	1	14.010	20.6	6.08	363	488	
79-01	55.3	14	28.280	9.57	22.3	1400	2270	
79-01	55.3	1	13.945	N A	5.38	414	577	
79-01	55.5	1	12.820	19.3	5.57	389	561	
79-01	55.5	1	10.971	20.6	5.55	393	507	
79-01	56.0	1	14.593	17.7	6.10	417	548	
79-01	56.0	10	25.397	8.84	16.9	1110	1710	
79-01	56.0	1	15.677	17.4	6.55	447	595	
79-01	57.0	1	10.018	18.6	9.21	653	915	
79-01	57.0	9	21.587	10.9	17.3	1160	1790	
79-01	57.5	1	8.804	23.9	8.28	574	824	
79-01	58.0	1	8.111	21.9	7.38	520	679	
79-01	58.3	1	8.141	20.6	8.07	563	784	
79-01	58.5	1	5.834	21.5	7.48	521	721	
79-01	61.0	1	1.193	16.5	8.64	564	788	
79-01	63.0	0	0.155	14.9	11.3	659	877	
79-01	65.0	0	0.060	15.3	7.79	467	465	

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
79-07	3.0	1	29.314	1.21	0.70	13.3	22	
79-07	3.0	5	29.326	1.26	0.70	14.7	26	
79-07	3.0	10	29.505	1.31	0.70	9.8	18	
79-07	3.0	25	29.927	0.50	0.90	4.5	4	
79-07	3.0	100	30.549	0.78	1.00	9.4	13	
79-07	3.0	200	30.789	0.45	2.70	10.7	4	
79-07	3.0	300	30.749	0.83	3.30	11.9	14	
79-07	3.0	350	30.769	3.11	4.10	15.8	23	
79-07	3.0	382	30.745	4.96	4.50	21.0	28	
79-07	3.0	392	30.769	8.43	8.70	25.9	27	
79-07	3.0	396	30.769	9.00	8.80	33.3	34	
79-07	3.0	398	30.771	8.76	9.20	31.5	45	
79-07	3.0	400	30.770	9.47	9.40	33.1	51	
79-07	3.0	401	30.769	8.95	10.5	37.6	60	
79-07	15.0	1	10.599	10.7	5.40	319	414	
79-07	15.0	5	29.161	1.19	0.30	5.0	11	
79-07	15.0	10	29.295	0.97	0.30	1.7	4	
79-07	15.0	25	29.906	0.31	0.60	2.8	2	
79-07	15.0	50	30.130	0.36	1.00	11.3	14	
79-07	15.0	75	30.265	0.74	1.30	39.0	74	
79-07	15.0	100	30.281	0.78	1.20	26.1	37	
79-07	15.0	150	30.355	1.59	4.40	48.5	78	
79-07	15.0	156	30.374	3.73	1.90	84.3	132	
79-07	15.0	166	30.493	4.06	1.60	79-2	128	
79-07	15.0	176	30.618	4.91	1.90	68.5	103	
79-07	15.0	180	30.648	6.43	2.30	91.2	118	
79-07	15.0	182	30.671	5.72	1.90	70.8	111	
79-07	15.0	184	30.692	5.58	2.20	79-3	122	
79-07	15.0	185	30.716	6.96	2.40	80.3	142	
79-07	56.3	0	2.676	10.6	10.2	545	834	

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
79-12	1.0	1	28.534	0.68	2.00	20.7	64	1.76
79-12	2.0	1	26.012	2.32	1.70	0.0	1	
79-12	3.0	1	24.789	3.38	1.30	0.0	11	
79-12	4.0	1	26.509	1.94	1.40	0.0	0	
79-12	5.0	1	22.220	5.70	1.10	7.1	24	
79-12	6.0	1	16.695	9.91	4.50	146	283	
79-12	7.0	1	15.177	10.7	5.60	263	457	
79-12	8.0	1	18.445	8.37	3.10	117	209	
79-12	9.0	1	18.613	8.62	1.90	74.0	134	
79-12	10.0	1	19.090	10.2	3.00	127	205	
79-12	11.0	1	27.222	1.18	1.20	0.0	0	
79-12	12.0	1	17.705	11.0	1.80	76.1	159	
79-12	13.0	1	15.682	13.4	5.20	260	468	
79-12	14.0	1	17.500	10.6	2.30	85.6	197	
79-12	15.0	1	13.082	9.66	19.0	69.7	1750	
79-12	16.0	1	11.933	15.9	23.7	101	2130	
79-12	17.0	1	20.316	8.02	2.10	84.6	180	
79-12	18.0	1	11.959	12.1	13.50	624	1180	
79-12	19.0	1	18.447	7.90	13.8	647	1170	
79-12	20.0	1	17.901	10.0	9.60	381	719	
79-12	21.0	1	18.249	8.97	5.60	287	491	
79-12	22.0	1	26.491	3.13	5.20	231	334	
79-12	23.0	1	25.472	3.87	3.40	181	249	
79-12	24.0	1	29.916	2.22	0.90	26.7	68	
79-12	25.0	1	22.618	5.83	3.20	119	211	5.10
79-12	26.0	1	25.377	4.18	1.40	45.0	88	
79-12	15.0	1	9.558	10.5	30.4	102	2670	27.2
79-12	15.0	1	11.747	12.7	19.10	51.3	1640	19.4
79-12	50.0	1	12.842	13.9	11.60	508	989	12.5
79-12	51.0	1	9.085	13.8	25.4	93.2	2270	26.9
79-12	51.0	1	12.280	14.4	8.40	364	634	9.06
79-12	51.0	1	16.544	10.8	4.60	227	392	8.34
79-12	51.0	1	16.061	10.6	5.00	198	359	8.57
79-12	52.0	1	7.481	6.91	63.9	2960	5560	87.1
79-12	52.0	1	8.176	6.13	91.3	333	8310	117.
79-12	52.0	1	3.154	9.30	232	10700	20500	287.
79-12	53.0	1	0.053	16.1	301	8180	13700	540.
79-12	53.0	1	0.563	18.0	248	13600	22200	530.
79-12	53.0	1	6.412	25.6	256	13700	22900	600.
79-12	53.0	1	0.054	17.4	286	13500	25200	368.
79-12	56.0	1	0.0	6.63	183	8150	16100	220.
79-12	59.0	1	0.0	5.27	233	11000	21100	274.
79-12	65.0	1	0.0	N A	188	10900	11500	209.
79-12	15.0	1	10.416	12.1	13.6	576	1120	14.7
79-12	15.0	1	10.267	12.5	16.1	673	1290	17.5
79-12	15.0	1	8.986	N A	15.2	636	1190	
79-12	15.5	1	6.294	9.55	54.6	2450	2280	63.1
79-12	15.0	100	30.590	N A	2.00	72.0	140	
79-12	50.0	1	11.400	14.6	11.9	520	968	13.3
79-12	52.0	1	5.890	5.97	140	6780	9540	171.
79-12	53.0	1	0.0	10.1	134	7730	6440	186.
79-12	53.0	11	30.027	6.26	13.9	566	1140	15.6

Cruise	Stn	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
79-12	53.3	13	29.610	6.13	151	6870	8410	236.
79-12	53.6	13	28.604	10.7	334	21500	35900	984.
79-12	54.0	14	28.143	12.4	790	37800	34600	1530.
79-12	54.3	14	27.887	11.1	525	25600	28100	929.
79-12	54.6	11	14.013	16.7	771	53200	20100	946.
79-12	55.0	11	0.0	5.33	207	8830	17200	285.
79-12	55.3	12	17.801	18.7	1360	63600	63700	2400.
79-12	55.5	11	0.0	4.83	175	7020	12000	296.
79-12	56.0	13	0.0	4.50	225	9630	16700	246.
79-12	56.6	10	0.0	N A	N A	N A	N A	309.

APPENDIX B.3 Time Series of Bottom Waters Collected at Station
56.3, Cruise 78-16 (Oct. 1978)

Date	Time	Depth (m)	Sal (ppt)	Dis Mn (ppb)	Part Mn (ppb)	Part Fe (ppb)	Part Al (ppb)	TSP (mg/l)
18	1115	11	26.969	3.62	6.30	431	569	8.33
18		11	22.925	12.6	5.60	501	583	8.75
18	1350	15	20.677	8.62	28.7	1750	2730	42.71
18	1425	9	11.859	8.55	46.6	2870	4700	56.08
18	1431	8	8.303	8.80	45.6	2930	5070	
18	1441	9	11.993	8.29	45.5	2830	4680	62.86
18	1500	8	11.023	9.77	45.9	2870	4560	62.82
18	1505	7	12.114	8.59	33.7	2170	3300	47.00
18	1522	7	12.558	8.75	30.4	1790	3240	40.12
18	1539	7	10.873	8.42	26.6	1620	2750	35.32
18	1556	7	9.810	8.27	24.1	1510	2420	30.24
18	1617	8	9.531	9.42	28.0	1710	2920	35.48
18	1624	8	8.658	9.51	34.0	2070	3440	43.67
18	1739	9	26.095	4.95	49.0	3100	5230	64.16
18	1753	9	26.740	4.28	37.8	2440	4220	51.32
18	1804	9	26.922	4.28	39.7	2460	4350	56.36
19	1151	9	26.530	2.67	4.50	236	380	5.60

APPENDIX B.4 Tidal Data for Steveston and Deas Island during
Cruise 78-16 (Oct. 1978)

Date	Tide Height at Point Atkinson (m)	Time at Steveston	Time at Deas Island
Oct. 18, 1978	1.1	0140	0225
	4.4	0805	0810
	2.7	1400	1430
	4.2	1910	1920
Oct. 19, 1978	1.1	0215	0300
	4.4	0900	0905
	2.8	1445	1505
	4.0	1950	2000

APPENDIX C Summary of Sediment Data

APPENDIX C.1 Dissolved Manganese Profiles in Interstitial Waters
 - Station 15 Sediments Collected Jan 12/78 and Feb 6/79

78-1-15		79-2-15	
Core Section (cm)	Dissolved Manganese (ppm)	Core Section (cm)	Dissolved Manganese (ppm)
0-3	1.82	0-3	3.02
3-6	3.85	3-6	4.81
6-9	3.15	6-9	3.19
9-12	2.87	9-12	2.95
12-15	2.64	12-15	2.58
15-18	2.59	15-18	2.12
18-21	2.36	18-21	1.61
21-24	2.17	24-27	1.28
24-27	2.02	31-34	1.01
27-30	1.98	38-41	1.12
30-33	1.88	45-48	0.85
33-36	1.85	52-55	1.21
36-39	1.64		
39-42	1.51		
42-45	1.19		
45-48	0.99		
48-51	0.71		

APPENDIX C.2 Dissolved Manganese Profiles in Interstitial
Waters of Estuarine Sediments Collected Feb 29/79

Station					
56.2		57.2		59.0	
Depth (cm)	Dis Mn (ppm)	Depth (cm)	Dis Mn (ppm)	Depth (cm)	Dis Mn (ppm)
0-3	4.61	0-3	0.077	0-3	35.5
3-6	7.50	3-6	0.048	3-6	37.0
6-9	10.9	6-9	0.126	6-9	----
9-12	6.58	9-11	0.087	10-13	25.0
12-15	4.82	11-14	0.019	13-16	19.0
15-19	3.28	14-17	0.019	16-19	7.7
19-22	6.30	17-20	0.048	19-22	5.6
22-26	6.27				

APPENDIX C.3 Complete Analyses of Estuarine Sediment from Cruise
79-12 (May 1979)

C.3.1 Total Acid Digestion Following an Ammonium Oxalate
Extraction

Station	Ammonium Oxalate Leachable Mn (ppm)	Ammonium Oxalate Resistant Mn (ppm)	Total Manganese (ppm)	Ammonium Oxalate Resistant Al (%)
3	---	804	---	7.30
15	70.8	275	346	4.74
53	153	371	524	5.44
54	74.0	477	551	5.48
55	72.2	519	591	5.03
56	102	366	468	5.29
59	130	350	480	5.48
65	125	384	509	5.21

C.3.2 Total Acid Digestion Only

Station	Mn (ppm)	Al (%)	Am. Ox. Res. Al as % of Total Al
3	1840	10.4	70
15	330	7.22	66
53	514	8.72	62
54	498	6.99	78
55	542	5.55	95
56	425	5.41	98
59	447	6.07	89
65	477	5.86	89

APPENDIX C.4 Dissolved Manganese and Salinity Profiles in
Interstitial Waters of Estuarine Sediments Collected in Jan 1980

Core Section	Station Number			
	57.2		62.5	
(cm)	Salinity (ppt)	Dis. Mn (ppb)	Salinity (ppt)	Dis. Mn (ppb)
0-3	28.2	75	6.8	25
3-6	24.0	75	2.9	N D ¹
6-9	21.5	40	3.5	N D
9-12	19.9	25	4.5	N D
12-15	19.2	N D	4.8	N D
15-18	17.9	N D	5.9	N D
18-21	18.1	45	6.7	N D
21-24	18.1	45	8.2	N D
24-27	18.9	N D	9.1	N D
27-30	19.7	N D	---	---
	59.0		62.2	
0-3	19.6	175	12.2	N D
3-6	13.7	100	10.0	N D
6-9	14.2	N D	8.9	N D
9-12	14.0	N D	8.5	N D
12-15	15.0	25	---	---

1. N D = not detected, concentration < 25 ppb

APPENDIX C.5 Complete Analyses of Estuarine Sediments
Collected in Jan 1980

Station & Core Section (cm)	Interstitial Water		Ammonium Oxalate Leachable Mn (ppm)	Ammonium Oxalate Resistant Mn (ppm)	Ammonium Oxalate Resistant Al (%)
	Salinity (ppt)	Dis. Mn (ppm)			
56.2					
0-3	26.6	---	80.2	316	4.46
3-6	23.0	0.88	111	434	5.08
6-9	24.4	3.2	106	352	4.98
9-12	24.2	4.4	142	442	6.21
12-15	25.6	4.2	178	425	5.86
15-18	25.8	3.0	243	472	6.95
18-21	26.0	2.3	218	430	6.26
21-24	26.8	4.7	212	413	5.68
24-27	22.8	5.7	93.5	395	5.62
27-30	20.5	4.6	81.9	373	5.59
60.5					
0-3	28.2	N D ¹	161	291	4.45
3-6	19.4	N D	---	---	----
6-9	17.8	N D	133	346	4.94
9-12	14.9	N D	---	---	----
67.0					
0-3	0.7	N D	168	293	5.21
3-6	0.9	N D	---	---	----
6-9	0.9	N D	156	347	5.38
9-12	0.9	N D	---	---	----
12-15	1.0	N D	---	---	----
15-18	1.1	N D	150	342	5.50
18-21	1.0	N D	---	---	----

1. N D = not detected, concentration < 25 ppb

APPENDIX C.6 Grain Size Data

Station Number	Section (cm)	% Sand	% Mud	Mean Grain Size (mm)	Standard Deviation
79-12-15	SS ¹	98.62	1.38	0.1842	0.6693
79-12-53	SS	89.53	10.47	0.1677	0.3569
79-12-54	SS	99.92	0.08	0.3424	0.7560
79-12-55	SS	99.69	0.31	0.2329	0.7436
79-15-56	SS	99.75	0.25	0.3045	0.6787
79-12-59	SS	99.93	0.07	0.2836	0.6933
79-12-65	SS	99.86	0.14	0.2938	0.7299
80-56.2	0-3	99.97	0.03	0.2353	0.7406
80-56.2	3-6	89.67	10.33	0.1789	0.3292
80-56.2	6-9	56.14	43.86	0.0225	0.0763
80-56.2	9-12	41.36	58.64	0.0109	0.0709
80-56.2	12-15	44.50	55.50	0.0125	0.0762
80-56.2	15-18	38.47	61.53	0.0094	0.0710
80-56.2	18-21	47.87	52.13	0.0174	0.0664
80-56.2	21-24	78.62	21.38	0.0993	0.1401
80-56.2	24-27	99.49	0.51	0.2983	0.7308
80-56.2	27-30	99.90	0.10	0.2940	0.7539
80-57.2	0-3	99.97	0.03	0.3936	0.7363
80-57.2	6-9	100.00	0.00	0.3472	0.7436
80-57.2	15-18	100.00	0.00	0.3724	0.7400
80-59.0	0-3	99.91	0.09	0.2774	0.7529
80-59.0	6-9	99.94	0.06	0.2643	0.7489
80-60.5	0-3	99.92	0.08	0.2335	0.7247
80-60.5	6-9	99.97	0.03	0.2287	0.7330
80-62.5	0-3	100.00	0.00	0.3648	0.7132
80-62.5	6-9	99.97	0.03	0.3603	0.6967
80-62.5	15-18	100.00	0.00	0.3900	0.6893
80-67.0	0-3	99.96	0.04	0.3589	0.7280
80-67.0	3-6	100.00	0.00	0.3545	0.7331
80-67.0	15-18	100.00	0.00	0.3551	0.7654

1. SS = Shipek Sample