



PERGAMON

Applied Geochemistry 15 (2000) 753–775

**Applied
Geochemistry**

Contrasting the geochemistry of suspended particulate matter and deposited sediments within an estuary

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Received 17 August 1998; accepted 24 August 1999

Editorial handling by R. Raiswell

Abstract

The geochemistry, as defined by amounts of easily reducible Mn (ERMn; Mn oxides), reducible Fe (RFe; Fe oxides), organic matter (% loss on ignition), total metal (Cu, Pb and Zn) and metals associated with the ERMn, RFe and organic matter components of deposited sediments (DS) and suspended particulate matter (SPM) were contrasted over a 1-year period (two-way ANOVA with sediment type and month as the two factors) within the Fraser River Estuary, BC, Canada. The geochemistry of SPM as compared to DS was distinctly different. The geochemistry of SPM displayed a marked seasonality. By contrast, seasonal differences in the geochemistry of DS were much less pronounced over the 12-month sampling period. Concentrations of organic matter and RFe in SPM were significantly greater (two-way ANOVA; $P < 0.05$) in winter months (maximums of 23% and 53 g kg⁻¹, respectively) as compared to the rest of the year (maximums of 9.3% and 11 g kg⁻¹, respectively). Concentrations of organic matter in DS did not change over the 12-month period; however, RFe in DS was significantly greater in winter months (7.3 g kg⁻¹) as compared to summer months (2.3 g kg⁻¹). Easily reducible Mn in both SPM and DS was highly variable throughout the year with no apparent seasonal dependence. Total concentrations of Cu, Pb and Zn and their partitioning among the 3 sediment components (i.e. ERMn, RFe and organic matter) were also month-dependent (two-way ANOVA, $P < 0.05$); metal concentrations in SPM were up to 17 times greater than DS with a higher proportion of these metals associated with the easily reducible component (oxides of Mn and amorphous forms of Fe oxides) during winter as compared to summer months. Trace metal concentrations and partitioning in DS showed the same seasonal trends, although not to the same degree as occurred for SPM, throughout the 4 seasons of study. Seasonal changes in the partitioning of metals in addition to greater proportions of the metal occurring in an easily reducible form in SPM relative to DS has potentially important implications for sediment ingesting organisms capable of filter-feeding on both SPM and DS. Specifically, metal bioavailability to sediment ingesting organisms from SPM may be seasonally dependent with periods of greatest exposure occurring during winter months, as compared to DS where no seasonal dependence occurs. To identify main vectors of metal exposure to sediment ingesting organisms, both the type of sediment and when they are feeding on the particular type of sediment need to be determined. © 2000 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

The behavior of metals in aquatic systems has been of increased interest due to the global anthropogenic

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alteration of trace metal cycles (Forstner and Wittman, 1981; Salomons and Forstner, 1984). Anthropogenic metals introduced into the aquatic environment occur either in particulate form or are rapidly sorbed to particles (Jenne and Zachara, 1987; Regnier and Wollast, 1993). Once sorbed, they contribute to the pool of metals associated with either suspended particulate matter (SPM) within the water column or are ultimately incorporated into deposited sediments (DS). For organisms that ingest either DS or SPM as a food source, these anthropogenic metals may cause severe adverse effects potentially leading to bioaccumulation by the organism and transfer via the food-chain to higher trophic levels.

The availability of anthropogenic metals to estuarine organisms is dependent on the presence of the trace metal (exposure), plus the nature of the geochemical component with which the trace metal is associated (Campbell and Tessier, 1989). The most important geochemical components considered to influence the bioavailability of metals to sediment ingesting organisms have been shown to be organic matter, Fe oxides, and Mn oxides (Luoma and Jenne, 1977; Tessier et al., 1984; Campbell et al., 1988; Bendell-Young and Harvey, 1991; Bendell-Young et al., 1994). For example, Rule and Alden (1996) and Thomas and Bendell-Young (1998) demonstrated under both laboratory and field conditions, that the accumulation of Cd by *Macoma balthica* was best related to Cd associated with the easily reducible fraction of sediment (i.e. Mn oxyhydroxides).

To date, the majority of studies directed at understanding the fate of metals in aquatic systems have focused primarily on the geochemistry of recently deposited sediments and the potential role of DS in providing a conduit for the transfer of metals from the sediment to sediment ingesting organisms (e.g. Campbell et al., 1988). However, due to their direct interface with the water, high surface area to volume ratio, and high nutritive quality (Hart, 1982; Ongley et al., 1982, 1988, 1992; Horowitz, 1986), SPM may represent an overlooked and possibly more chemically and biologically relevant metal source for sediment ingesting organisms, as compared to DS. Furthermore, in contrast to DS, SPM is found in a much more dynamic environment, experiencing profound seasonal changes in physico-chemical variables such as temperature, pH and salinity, which have the potential to alter the geochemistry of SPM and hence affect metal bioavailability.

Potential differences in the geochemistry and metal bioavailability of SPM and DS are important in relation to the sediment ingesting organisms capable of exploiting both types of sediment as potential food sources (see Miller et al., 1992 for a review). For example, the suspension-feeding bivalve *Mya arenaria*,

which maintains its inhalant siphon flush with the sediment surface feeds on surface sediments as well as suspended sediment (Rasmussen, 1973). In addition, some species of polychaetes have the ability to switch feeding modes depending on the flux of suspended particulates (Taghan, 1983). If metal bioavailability is dependent on sediment geochemistry (e.g. Campbell et al., 1988; Thomas and Bendell-Young, 1998), then metal availability to sediment ingesting organisms may potentially differ between DS and SPM, and differences may be seasonally dependent.

Hence, the objective of this study was to characterize and contrast the geochemistry of DS and SPM within an estuarine environment over a one-year period. Geochemical properties of the two sediment types which were contrasted include; particle size, organic content, concentrations of Fe and Mn oxides, total Cu, Pb and Zn concentrations, and the amounts of Cu, Pb and Zn partitioned onto organic matter and Fe and Mn oxides. Ultimately, this information will allow for better prediction of where (i.e. DS versus SPM) and when (i.e. season) sediment ingesting organisms capable of exploiting both sources of sediment as a food resource are at greatest risk to metal exposure via their diet.

2. Methods

2.1. Study area

The Fraser River drains an area of approximately 230,000 km² (25% of British Columbia land mass; Dorcey and Griggs, 1991). River discharge varies from 400 m³ s⁻¹ (just prior to the spring snowmelt) to as great as 15,000 m³ s⁻¹ (in June following a rapid snowmelt), with an average of approximately 3475 m³ s⁻¹ (Kennett and McPhee, 1988). Of the total discharge into the Strait of Georgia, the North Arm discharges 16%, 70% flows past Steveston and the remaining 14% is discharged through Canoe Passage (Fig. 1). Most of the sediment transport occurs during the spring snowmelt (the freshet); suspended particulate concentrations can reach mean values of 400 mg L⁻¹, with near-bottom concentrations approaching 1000 mg L⁻¹ (Milliman, 1980). The Fraser River carries a large suspended particulate load and as a result, the sedimentary material of the upper and mid estuarine regions is dominated by riverine input. A detailed study on the sediment transport in the Fraser River (McLaren and Ren, 1995) identified that, in the lower Fraser River, mud is accumulating (e.g. zones of net accretion) with total deposition (once deposited there is no further transport) occurring in backwater regions (Fig. 2).

The 3 study sites were located in the lower reaches

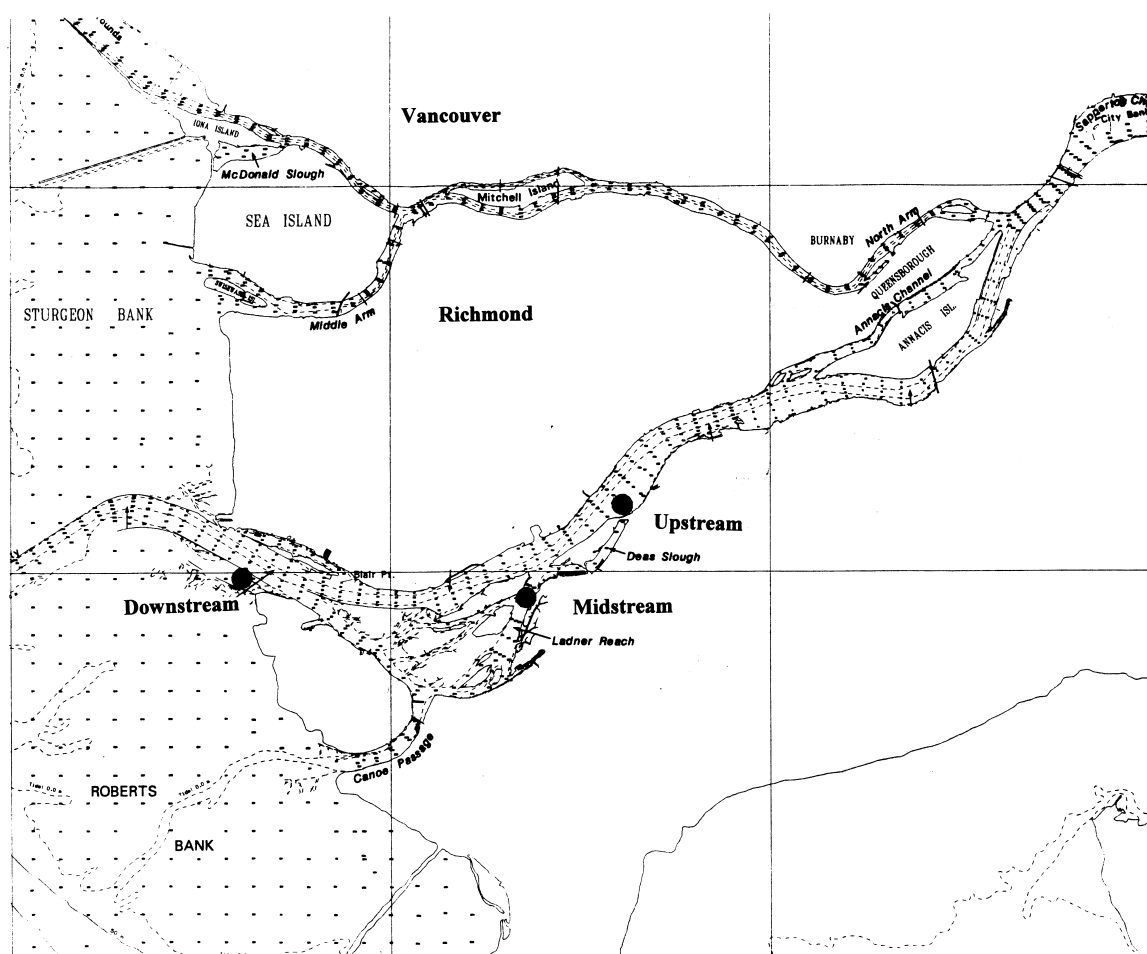


Fig. 1. Study region and the location of the 3 sampling sites.

of the South Arm the upstream and midstream sites within regions of mud accretion and the downstream site within a region of total deposition (Fig. 2). Approximately 10 km upstream from the 3 study sites, is the Annacis Island Sewage Treatment Plant which is the single largest sewage outfall into the south arm of the Fraser River (FREMP 1996; Fig. 1). It discharges on average $4.32 \text{ m}^3 \text{ sec}^{-1}$ of primary treated sewage into the South Arm of the Fraser River (FREMP 1996), accounting for 0.5 and 0.06% of the total discharge during periods of low and high flow, respectively.

2.2. Sediment sampling

Collection, laboratory processing and analysis of Fraser River Estuary sediments was undertaken monthly (with the exception of February) at each site over the course of one year (August 1994 to August 1995). At each site, water containing suspended sedi-

ments was collected in pre-washed 20-L plastic buckets, with field rinses according to APHA (1992). To collect the evenly distributed $<63 \mu\text{m}$ fraction (Ongley et al., 1982; Horowitz et al., 1990), near surface water was collected on mudflats with a water depth of 1.5 m. Visible resuspensions were carefully avoided. Three replicates of 10 buckets each ($3 \times 200 \text{ L}$) and 3 sediment cores (using a Wildco[®] hand corer) were taken at each site. The oxic (surficial) portion of these cores (above the visible redox colour change) were transferred to acid-washed glass jars for transport to the laboratory for subsampling and analyses. The oxic portion generally varied from 2 to 8 cm depth. Concurrent data recorded using a Hydrolab[®] Surveyor II (which had been fully calibrated prior to field employment) included temperature, pH, dissolved O_2 , conductivity, Eh, and salinity. Fraser River discharge data was provided by the Water Survey of Canada.

Samples were immediately transported to the laboratory where they were kept refrigerated at 5°C until

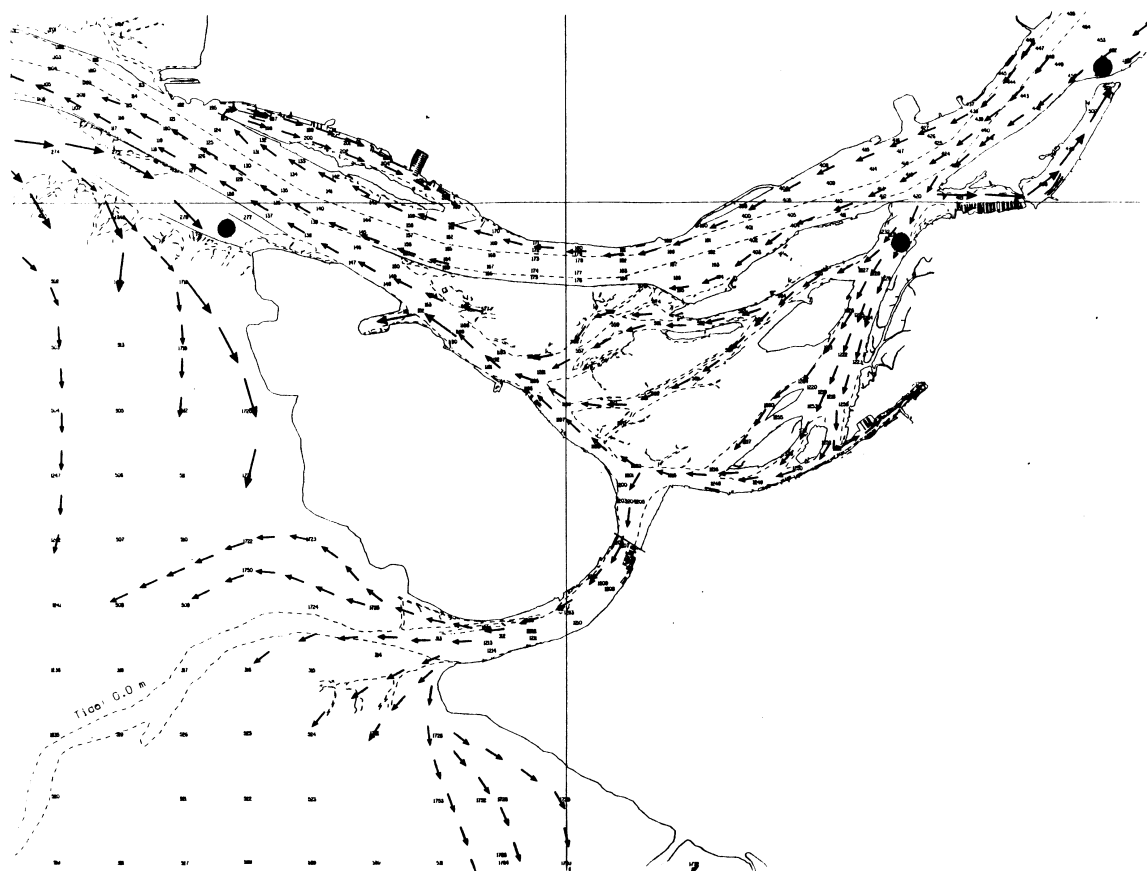


Fig. 2. Zones of accretion and deposition relative to the 3 sampling sites within the lower Fraser River Estuary (McLaren and Ren, 1995). Small arrows are zones of accretion; large arrows are zones of total deposition. Sample sites are as denoted in Fig. 1.

processing (always within 72 hr). SPM was separated from the 200 L water samples with close to 100% efficiency by flow through centrifugation at 15000 rpm, using the Sorvall[®] TZ-28 system in GK continuous flow mode in a Sorvall[®] RC5C Centrifuge with a flow rate of between 0.6 and 0.75 L min⁻¹. Continuous-flow centrifugation has been used by many researchers to separate SPM from natural waters (e.g. Ongley et al., 1982; Horowitz et al., 1990). Ongley et al. (1990) found that at a flow rate of 6 L min⁻¹ recovery efficiency was 90–95% in the fall, but fell considerably in the summer (to as low as 15%) as the organic content of the SPM rose. That is as the specific gravity of the SPM decreased, separation becomes less efficient. Overall, the separation efficiency of various flow-through centrifuge systems has been found to be greater than 90% for particles over 0.25 µm (Santiago et al., 1994). Five subsamples of each of the 3 replicates of SPM and DS were placed into acid-washed 50 mL centrifuge tubes and weighed (to the nearest 0.001 g). In addition, the total SPM recovered by centrifugation

was recorded. Samples were simultaneously (each sediment component treated individually with a selective extractant rather than sequentially where only one sediment sample is used for all extractions) extracted following the methods of Bendell-Young et al. (1992; Fig. 3) which separates sediment into 4 operationally-defined components; (1) easily reducible Mn and Fe (Mn oxides and amorphous forms of Fe oxides) and associated metals (ERMn, ERZn, ERCu and ERPb), (2) reducible Fe (crystalline Fe oxides; RFe) and associated metals (RCu, RPb and RZn), (3) metals associated with organic matter and (4) residual metals.

In the extraction scheme of Bendell-Young et al. (1992), separate subsamples of sediment are used to determine the 4 operationally-defined metal associations. As a result, the first extract, the easily reducible metal, removes metals associated with oxides of Mn and amorphous Fe oxides, whereas the second extract, the reducible metal, removes both the easily reducible metal and the reducible metal. To obtain those metals associated with just the reducible fraction (R metal),

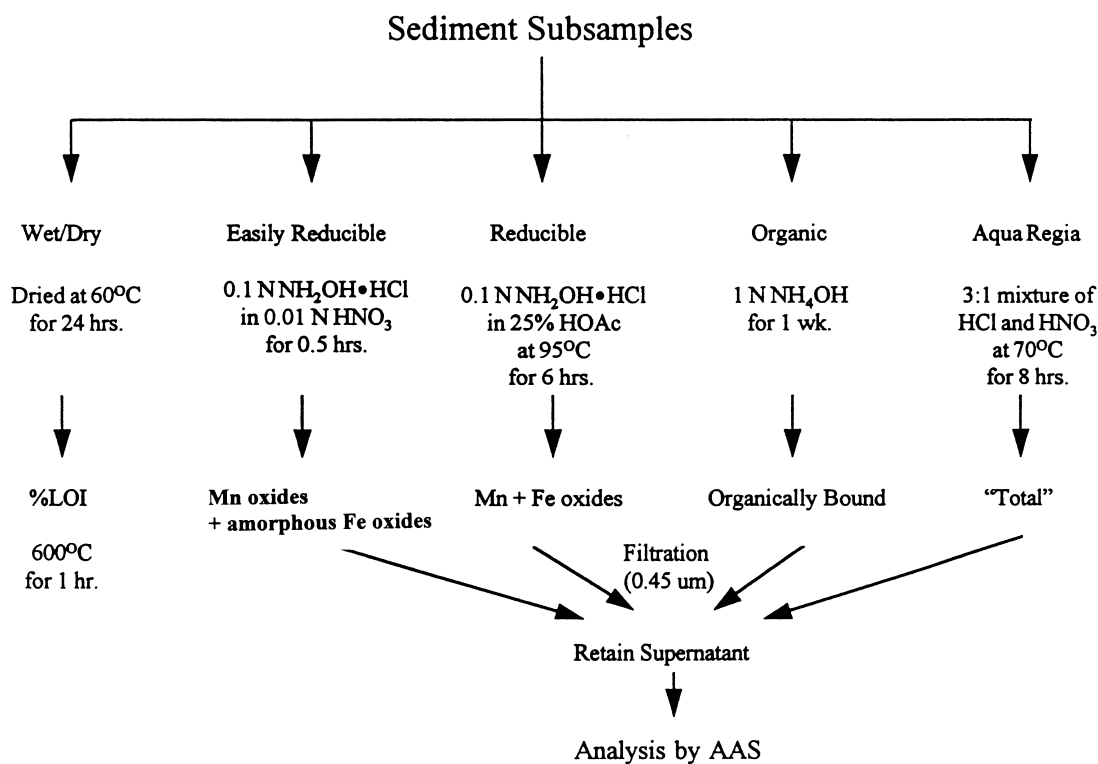


Fig. 3. Simultaneous extraction scheme of Bendell-Young et al. (1992) used for determining metal partitioning in suspended and deposited sediments.

amounts of metal recovered from the more severe second extract were subtracted from metals recovered from the first extract. Metals associated with organic matter are simply those recovered by the alkaline extract. To obtain concentrations of residual metal, amounts of metal recovered from the first 3 extracts were subtracted from metals recovered from the aqua regia digest. Total metal was the sum of metal recovered from the 4 fractions (of note; this “total” will not include some resistant silicates).

Organic content was determined by loss on ignition (%LOI) at 600°C for 1 hr in a blast furnace. This procedure assumes that the difference in weight before and after ignition of the dried sediment is primarily due to loss of organic C in sediments. As sediments are dried to a constant weight prior to combustion, errors introduced due to the dewatering of clays should be relatively insignificant. Carbonates in estuarine and marine sediments may also contribute to %LOI values. However, this mineral occurs primarily as large components (e.g. broken shells) (Thomas and Bendell-Young, 1998), which were not included with collected sediment. All subsamples were treated with a 15 to 1 ratio of analytical-grade (Baker Instra Analyzed or BDH Analar) extractant to sediment. Supernatants

were removed from the extraction tubes through Millipore Millex-HV sterilizing filter units (0.45 µm) using acid washed 10 mL syringes. Chemical analyses were carried out by flame atomic absorption spectrophotometry (FAAS) on a Perkin-Elmer® 1100B FAAS following standard optimization procedures. Limits of detection were 0.01 mg L⁻¹ for Fe, Mn, Cu, and Pb and 0.03 mg L⁻¹ for Zn. Concentrations of metals were well above detection limits in all cases and for Fe and Mn 1 to 10 dilutions were required to bring the sample within analytical range. Quality assurance/quality control (QA/QC) was assured through inclusion of NRC reference standards (MESS-2) and reagent blanks. Reference standards were within 10% of certified values. Precision of all analysis was always less than 5%.

SPM particle size was determined in triplicate using a model T_A Coulter Counter® with an aperture of 100 µm. Particles suspended in a 3% NaCl solution were counted for 5 seconds. DS particle size was determined by hydrometer which, based on Stokes Law, separates particles into % sand (<62.5 µm), silt (between 2.0 and 63.5 µm) and clay (<2.0 µm). This method could not be used with SPM due to sample size requirements (40 g). Particle size analysis was conducted on sedi-

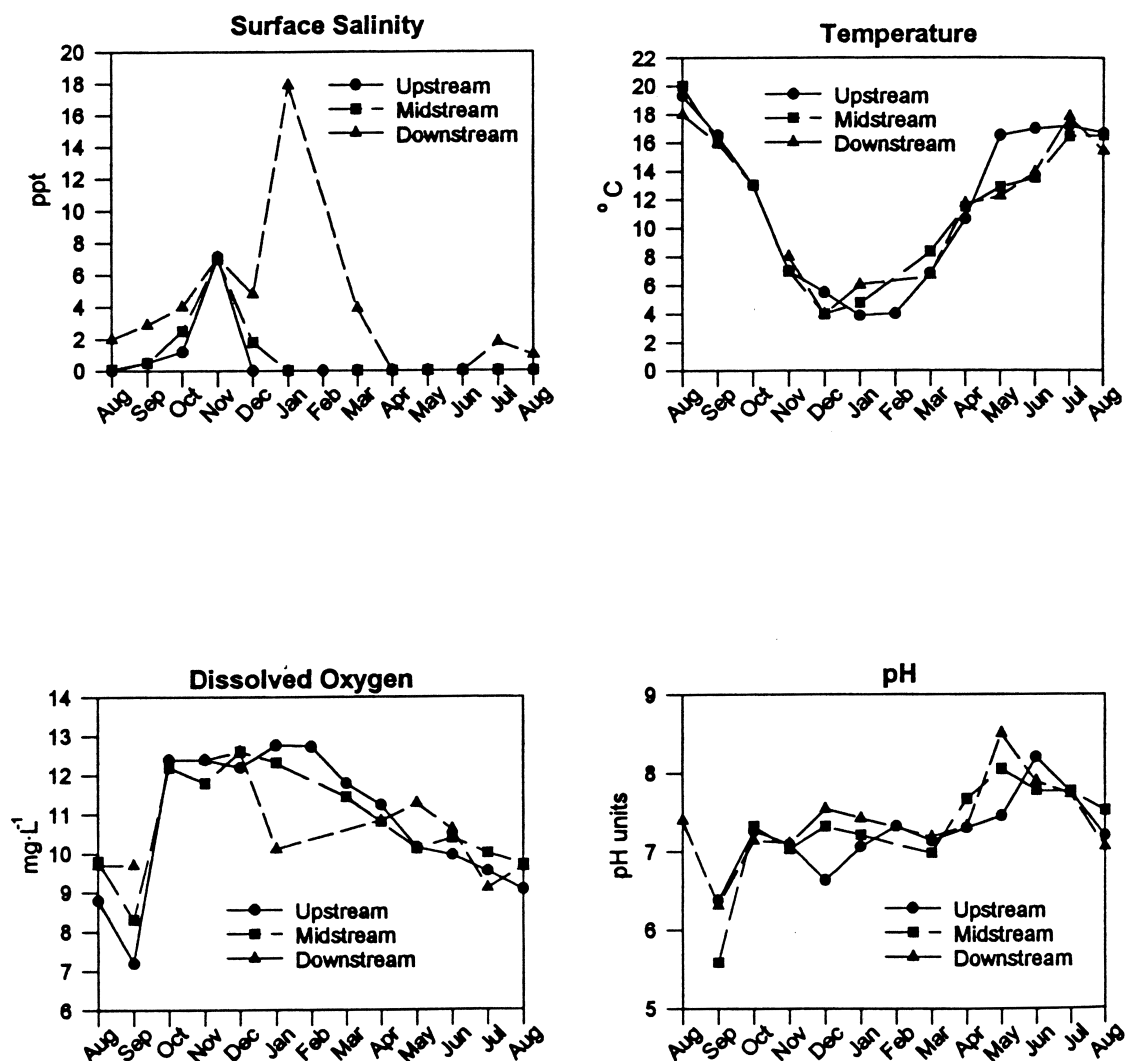


Fig. 4. Salinity, temperature, dissolved O₂ and pH at the 3 sites for the 12-month study period.

ment suspensions of composites of the 3 DS cores collected per site.

Statistical analyses of the geochemical characteristics of the two types of sediments were carried out using SAS, version 6.08 (SAS, 1990). Significance of all tests was accepted at $P < 0.05$. Characteristics included in the analysis were: organic matter (%LOI), easily reducible Mn (ERMn), reducible Fe (RFe), total trace metals (Cu, Pb, Zn), trace metals associated with the 4 components (i.e. easily reducible and reducible metals, metals associated with organic matter and residual metals), plus the proportion of metal partitioned to the first 3 components. The proportion (in %) is the amount of metal recovered from a particular com-

ponent divided by the amount of metal recovered from the 4 components (total metal) multiplied by 100.

Sediment geochemistry was independent of sampling site (ANOVA; $P > 0.05$). Therefore all 3 sample sites were pooled for further analysis. Comparisons in the sediment geochemistry of SPM relative to DS, among months and the interaction between sediment type and month were determined through a two-way ANOVA (with sediment type and month as the two factors). Where significant differences were detected, Tukey's multiple contrasts were used to determine where the significant differences occurred. In all analyses, proportional data was arcsine transformed. Simple Pearson product correlation coefficients were used to

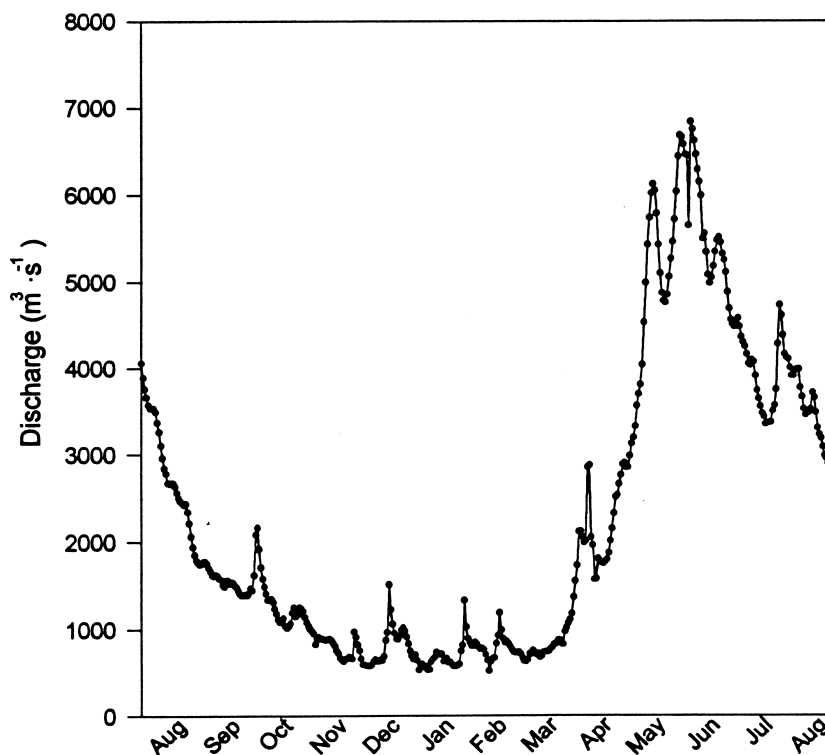


Fig. 5. Discharge versus month for the Fraser River Estuary.

determine relationships between the physico-chemical parameters of T, salinity, pH, dissolved O₂, flow rate and SPM concentration.

3. Results

3.1. Physico-chemical

Salinity, temperature, dissolved O₂ and pH were measured over the period of August 1994 to August 1995 at each site and, with the exception of salinity, showed minimal difference among the 3 sites (Fig. 4). Fraser River discharge showed normal seasonal variation, with storm events occurring over shorter time scales (Fig. 5).

3.2. SPM concentration

SPM concentration was similar for the 3 sites (Fig. 6). Unsurprisingly, SPM concentration was highly correlated with discharge, ($r = 0.77$; $P = 0.0001$, $n = 36$) (Fig. 7). Because of the co-correlation between discharge and SPM concentration, the actual discharge of SPM per unit time was the same (10 mg s^{-1}) under

both low and high conditions for the months of December and June, respectively.

3.3. Particle Size

The weighted mean particle size of SPM at all 3 sites was $11.26 \mu\text{m} \pm 2.5$ (S.D.) ($n = 9$) (Fig. 8a–c). This is consistent with previous observations which note that in general the SPM particle size population (especially the permanently suspended surface and near surface layers) is uniform (Ongley et al., 1982; Horowitz et al., 1990). Of the 3 size fractions used to characterize the DS, % silt was always the dominant fraction comprising close to 30–80% of the total (Fig. 9a–c). No statistically significant differences between the percentages of either clay or sand were found among the 3 sites, although significant intersite differences were noted for %silt (ANOVA; $P = 0.005$, $n = 33$), with the mid-stream site having a higher proportion of silt relative to the other two sites.

3.4. Geochemical matrix (organic content, ERMn and RFe)

Organic content and the concentrations of Mn oxides (ERMn) and Fe oxides (RFe) in the SPM and DS

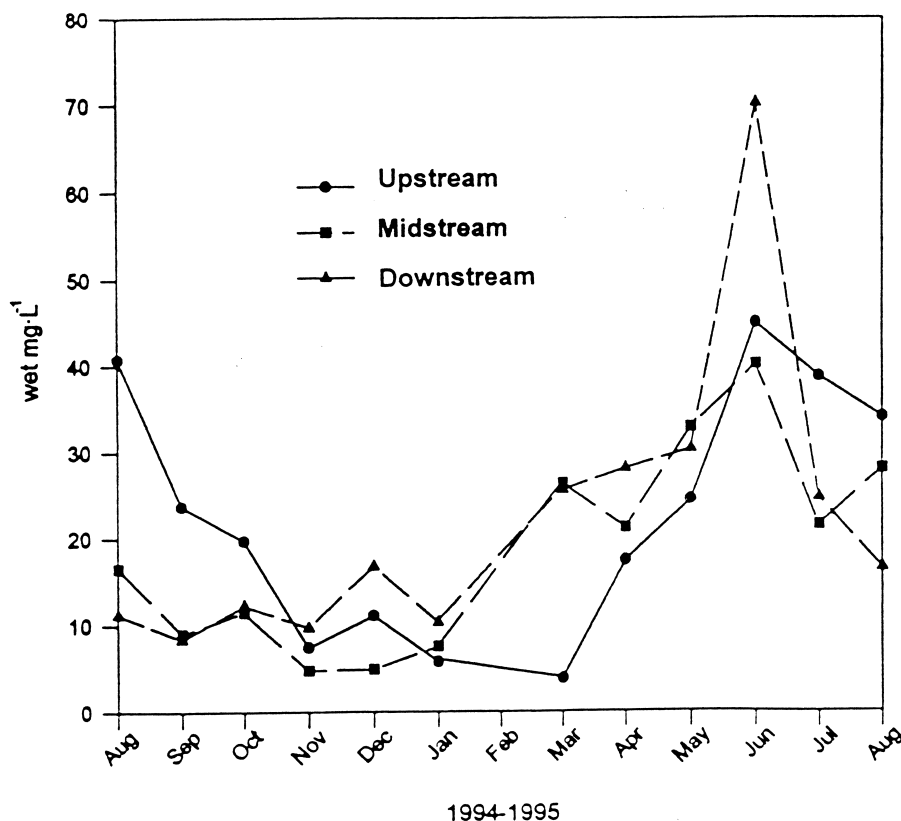


Fig. 6. SPM concentration versus month for the Fraser River Estuary.

of the Fraser River Estuary are summarized in Fig. 10a–c. Concentrations of organic matter, ERMn and RFe recovered from the two sediments were dependent on sediment type, month and the interaction between sediment type and month ($P < 0.0001$; two-way ANOVA). (In a two-way ANOVA, the interaction term accounts for the dependence of the effect of one factor (e.g. sediment type) on the level of another factor (e.g. month). This interactive effect can be either negative (interference) or positive (synergistic)).

3.5. Organic matter (%LOI)

In general, %LOI for SPM was greater than %LOI for DS with differences most apparent for the months of November to May (Fig. 10a). Organic matter for SPM was significantly greater in January and December as compared to July, August/94, September and October. In contrast to SPM, no seasonality was noted for %LOI in DS (Table 1). Importantly, the estimated contribution of organic matter originating from the Annacis Island Sewage Treatment Plant to the seasonal trends in SPM %LOI was only 1.12 and 0.6% under low and high flow conditions, respectively. This

estimated contribution was calculated as follows: The effluent from the treatment plant contains 48% or 480 g L⁻¹ total organic C (Sylvestre et al., 1997). The organic matter content of SPM is approximately 5% or 50 g L⁻¹ and 23% or 230 g L⁻¹ under high (June) and low (December) flow conditions, respectively (Fig. 10a). Discharge under high and low flow conditions for the south arm of the Fraser River is 7000 and 800 m³ s⁻¹, respectively (Fig. 5) and discharge from the treatment plant is 4.32 m³ s⁻¹ (FREMP 1996). Therefore the Fraser River discharges approximately 3.5×10^8 g s⁻¹ and 1.8×10^8 g s⁻¹ of organic matter under high and low conditions, respectively. The Annacis Island Sewage Treatment Plant discharges approximately 2.07×10^6 g s⁻¹ of organic matter, throughout the year. Thus, the contribution of the sewage treatment plant to the overall %LOI content of SPM can be estimated at 1.12 and 0.6% for low and high flow conditions, respectively.

3.6. RFe (Fe oxides)

Concentrations of RFe associated with SPM were always greater than those of DS (Fig. 10b). Reducible

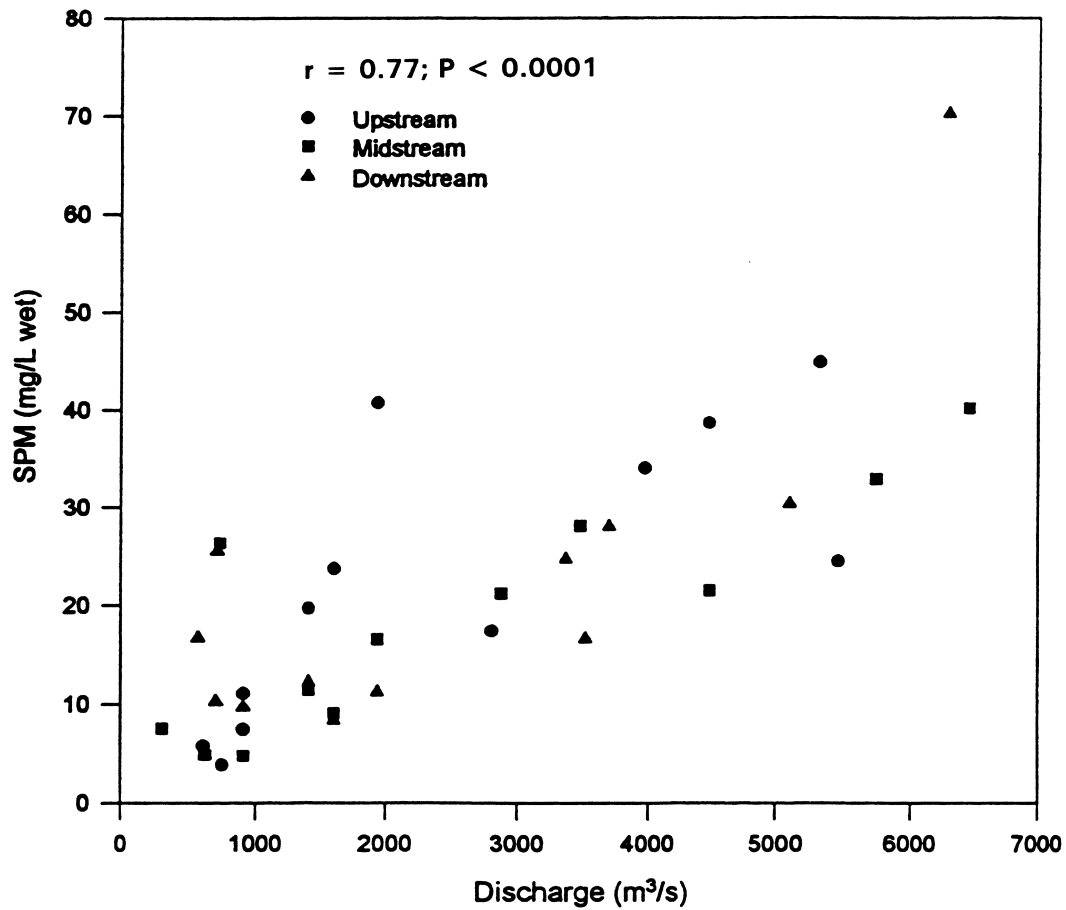


Fig. 7. Relationship between discharge and SPM in the Fraser River Estuary (1994–1995).

Table 1

Summary of significant differences ($P < 0.05$; Tukey's) in the geochemical matrix (i.e. organic matter (%LOI), RFe and ERMn) of SPM and DS by month. Those months that are significantly different from each other are indicated by a unique letter^a

	%LOI/SPM	%LOI/DS	RFe/SPM	RFe/DS	ERMn/SPM	ERMn/DS
Month	jan a	NS	jan a	mar a	jan a	au95 a
	dec ab		nov a	jan ab	may ab	jul ab
	mar abc		mar ab	dec abc	nov ab	apr ab
	may bcd		dec ab	nov abcd	au95 ab	may ab
	nov bcd		apr bc	apr abcd	jul ab	nov ab
	apr bcd		oct bc	jun abcd	oct ab	jan ab
	au/95 bcd		au95 bc	may abcd	dec ab	jun ab
	jun bcd		may c	au95 abcd	jun ab	dec ab
	oct cd		au94 c	jul bcd	apr ab	oct bc
	jul cd		jun c	sept cd	mar b	mar bc
	sep d		jul c	oct d	sep c	au94 c
	au94 d		sep c	au94 d	–	sept c

^a NS: no significant differences among months. SPM: suspended particulate matter, DS: deposited sediment.

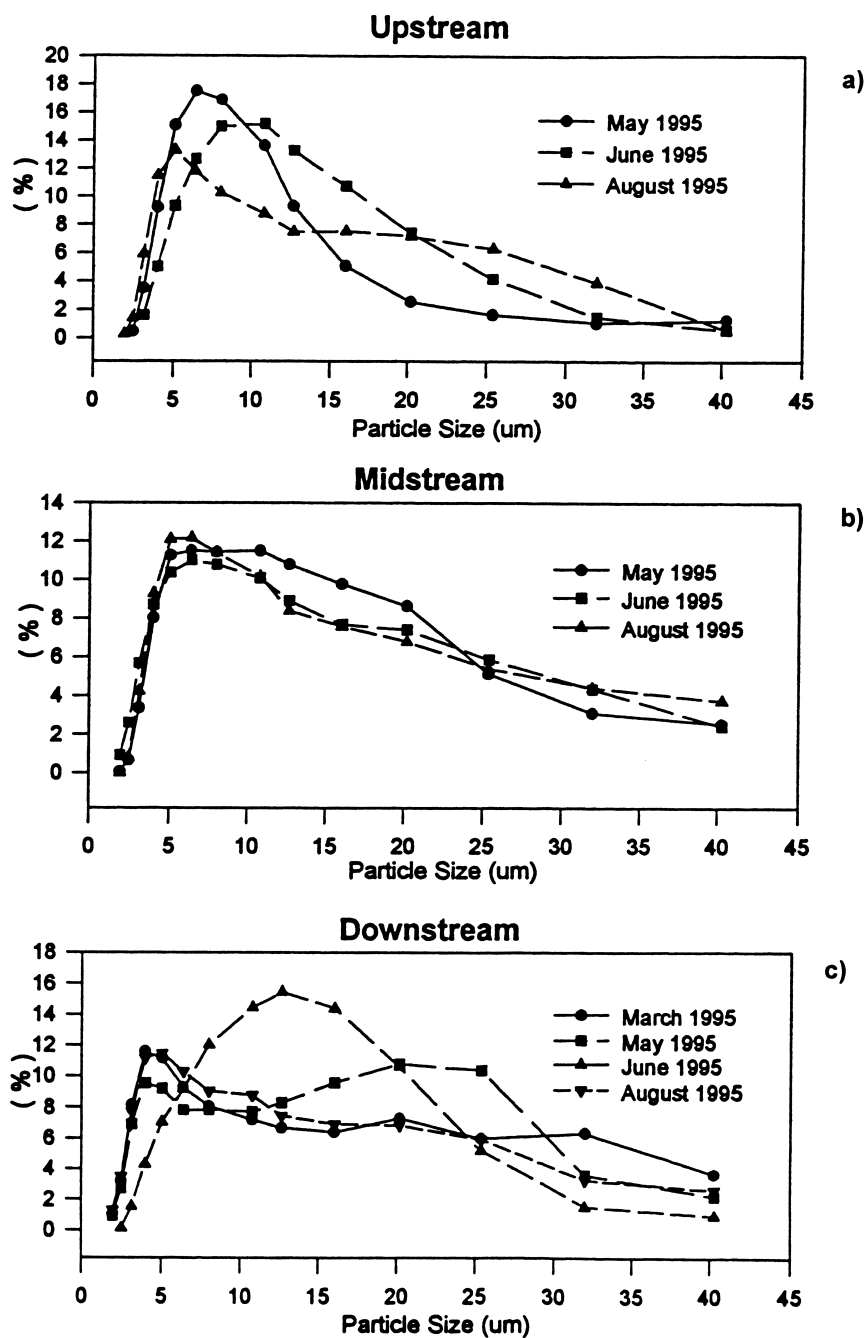


Fig. 8. Particle size distribution for SPM taken at the 3 study sites for the months of May, June and August.

Fe content for each sediment type was dependent on month, with winter months (November to March) containing significantly greater amounts of RFe as compared to summer months (May to September for SPM and May to October for DS) (Table 1).

3.7. ERMn (Mn oxides)

ERMn concentrations varied considerably over the course of the sampling period (Fig. 10c). However, in contrast to RFe and organic matter, this variation in

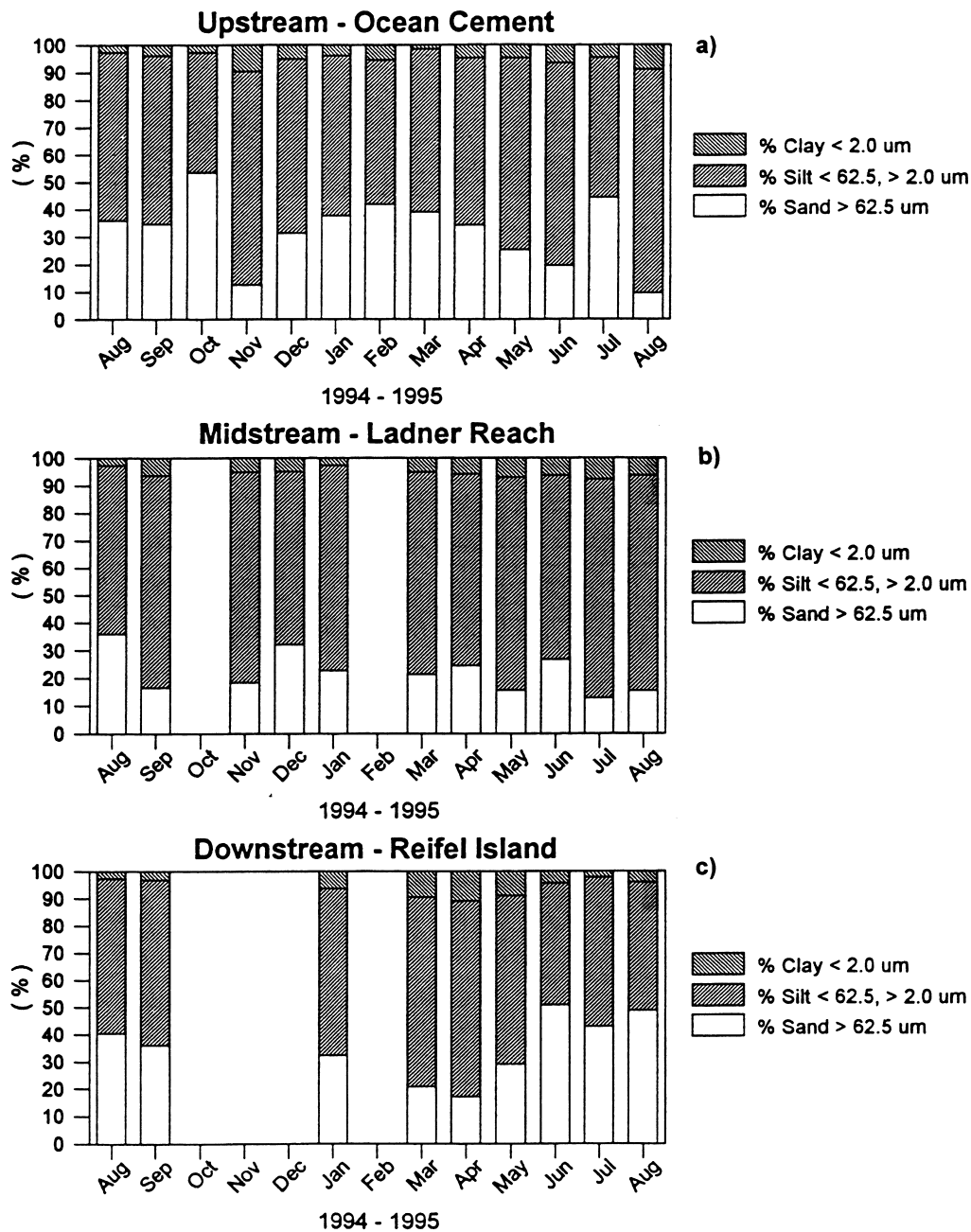


Fig. 9. Particle size distribution for DS at the 3 study sites.

ERMn concentration for the two sediment types was independent of season (Table 1, Fig. 10c). Concentrations of ERMn in SPM were generally greater than DS.

3.8. Total metal concentrations

Total concentrations of Cu, Pb and Zn for the two

sediment types over the 4 seasons of study are summarized in Fig. 11a–c. These metals show similar trends to those observed for organic matter and RFe. With the exception of Cu and Pb in DS, metal concentrations were significantly different between sediment types, among months and the interaction between month and sediment type (two-way ANOVA, $P < 0.0001$; Table 2). Total metals were always significantly

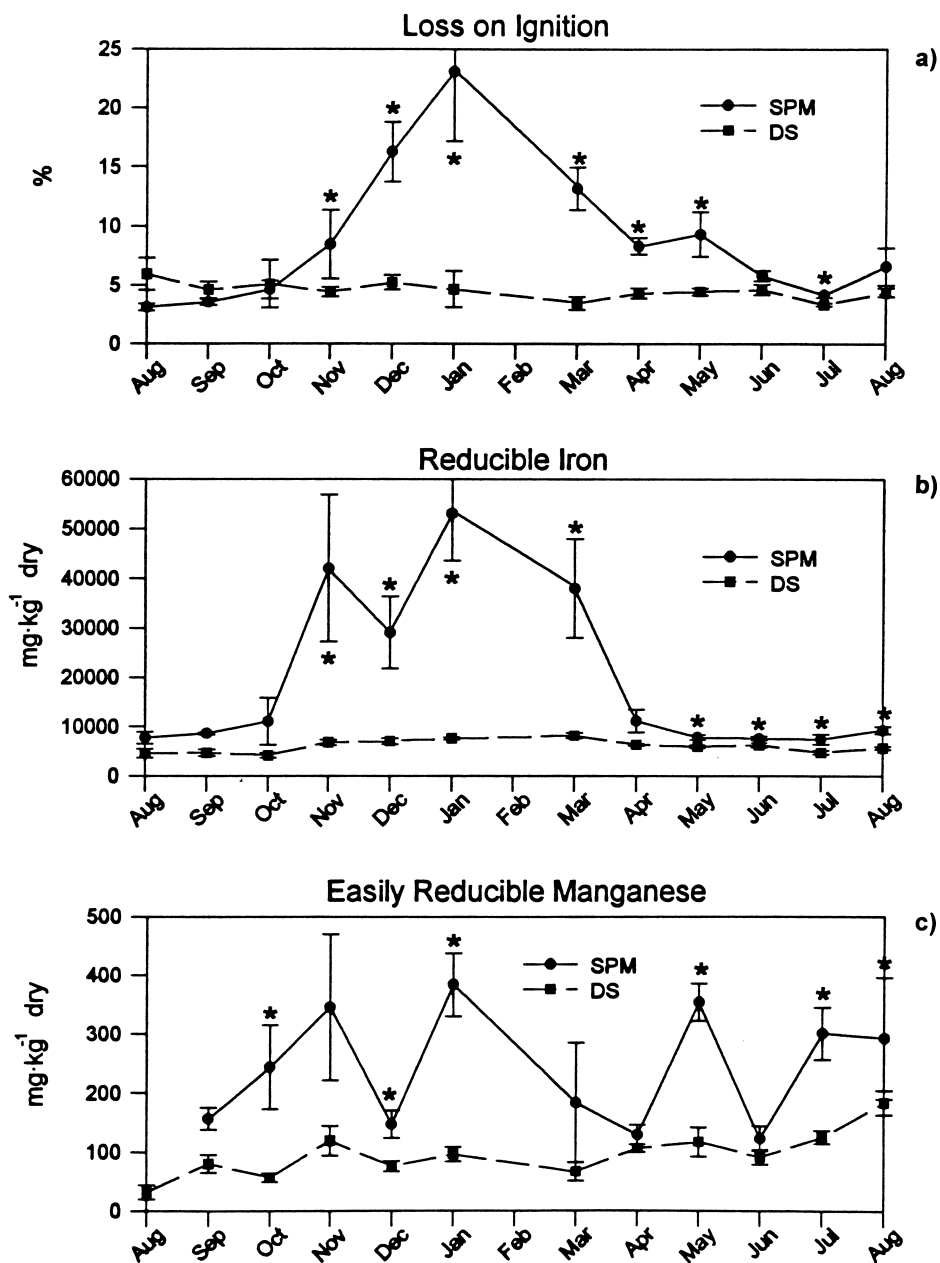


Fig. 10. Average (± 1 S.D.; $n = 9$) for (a) loss on ignition, (b) reducible Fe and (c) easily reducible Mn versus month for the Fraser River Estuary. Asterisks denote when SPM is significantly different from DS (two-way ANOVA).

greater in SPM as compared to DS with maximum concentrations for all metals in SPM occurring throughout the period of low flow (November through to March). Concentrations of total Cu and Pb in DS were similar among the 4 seasons sampled. Total Zn in DS was significantly greater in the months of June, July, August, October, and November as compared to the months of December, April and May (Table 2).

3.9. Metal partitioning; concentrations

Metal concentrations determined in the 4 fractions over the sampling period are summarized in Figs. 12–14. Two way-ANOVA indicated significant differences (Table 3) between sediment type, among months, plus the interaction term between month and sediment type for all metals in all phases except for the following; the

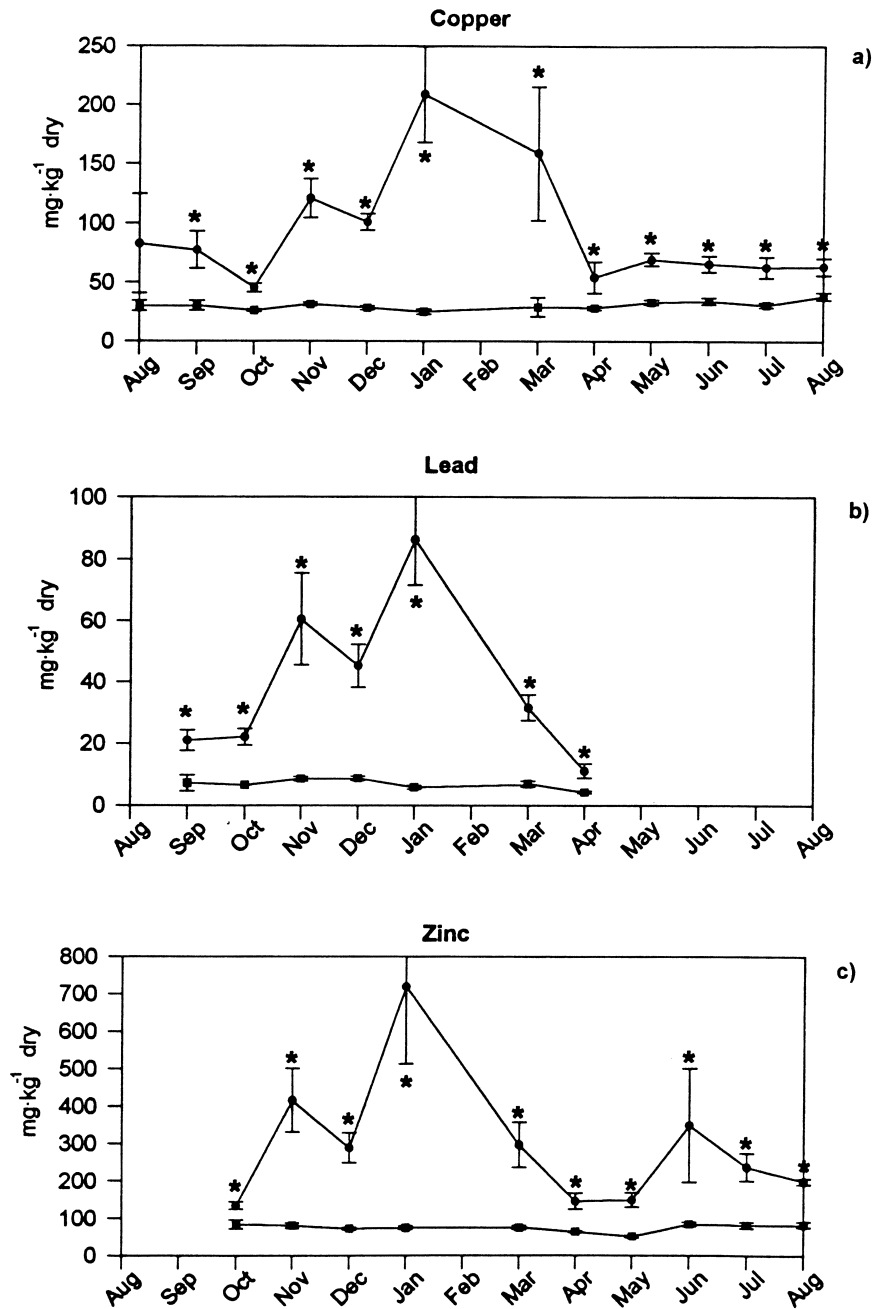


Fig. 11. Average (± 1 S.D.; $n = 9$) for (a) total Cu, (b) total Pb and (c) total Zn versus month for the Fraser River Estuary. Asterisks denote when SPM is significantly different from DS (two-way ANOVA).

interaction between month and sediment type (reducible Pb), sediment type (reducible Zn), and for month and the interaction between month and type (residual Zn). Metal concentrations in the 4 phases were always greater in SPM versus DS (Figs.12–14 for Cu, Pb and Zn, respectively).

3.9.1. Copper

Copper concentrations in the easily reducible and organic phases were an order of magnitude higher in SPM versus DS (Fig. 12). In the present study, differences were most apparent in the months of January and March, coincident with lowest flows and higher

Table 2

Summary of significant differences ($P < 0.05$; Tukey's) in the total metal content of SPM and DS among months where metals are Cu, Pb and Zn. Those months that are significantly different from each other are indicated by a unique letter^a

	Cu/SPM	Cu/DS	Pb/SPM	Pb/DS	Zn/SPM	Zn/DS
Month						
jan a	NS	jan a	NS	jan a	jun a	
nov ab		nov ab		nov ab	oct a	
mar ab		dec ab		dec abc	aug a	
dec ab		mar abc		mar abc	jul a	
sept ab		oct bc		jun abc	nov a	
may ab		sept bc		jul bc	mar ab	
jun ab		apr c		aug bc	jan ab	
au95 ab				may c	dec b	
jul ab				apr c	apr b	
au94 b				oct c	may b	
oct b						
apr b						

^a NS: no significant differences among months.

concentrations of suspended particulate organic matter and reducible Fe. In addition to the notable differences in Cu concentrations observed between SPM and DS, a distinct seasonal pattern was evident in SPM Cu concentrations. Copper concentrations in the easily reducible and organic phases of SPM reach a maximum of 141 ± 28 and 140 ± 57 mg kg⁻¹ in January and March, respectively, with these two phases comprising the majority of the Cu present (Fig. 11). Maximum Cu concentrations in the easily reducible and organic phase of DS were 10.9 ± 1.62 mg kg⁻¹ and 7.17 ± 1.45 mg kg⁻¹ in January and April, respectively.

3.9.2. Lead

Lead was not detected in the organic phase in either SPM or DS. Otherwise, Pb concentrations were an order of magnitude higher in SPM compared to DS with significant differences in concentrations among the 3 components occurring between sediment type and among months (Fig. 13; Table 3). A seasonal pattern was also noted for total SPM Pb; concentration maxima for Pb in SPM were observed from November through March (Fig. 13). Concentrations of Pb in the easily reducible phase comprised the major portion of the total sediment Pb throughout the months of October to January with a maximum of 61.6 ± 16.1 mg kg⁻¹ occurring in November. Concentrations of easily reducible Pb in DS were also the greatest during November, albeit at much lower levels (4.3 ± 0.4 mg kg⁻¹).

3.9.3. Zinc

Zinc concentrations in all phases were in general an

Table 3

Two-way ANOVA for differences in concentrations of metals recovered from the 4 phases with sediment type and month as the 2 factors. ER: Easily reducible metal, R: reducible metal, O: organically bound metal, RES: residual metal (*: significant at $P < 0.05$. ns: not significant. –: no comparison possible)

Phase	Copper				Lead				Zinc			
	ER	R	O	RES	ER	R	O	R	ER	R	O	RES
Month	*	*	*	*	*	*	–	*	*	*	*	ns
Type	*	*	*	*	*	*	–	*	*	ns	*	*
M*T ^a	*	*	*	*	*	ns	–	*	*	*	*	ns

^a M * T = month * type..

order of magnitude greater in SPM than in DS and also displayed a strong seasonal dependence (Fig. 14; Table 3), with concentration maxima in SPM observed from November through to March. Concentrations of Zn in the easily reducible and organic phases were the major phases contributing to the total concentrations. Zinc in the easily reducible phase of SPM reached a maximum of 686 ± 480 mg kg⁻¹ in November, whereas easily reducible Zn concentrations in DS reach maxima of 17.8 ± 9.7 mg kg⁻¹ in May. Zinc in the organic phase reached a maximum of 607 ± 160 mg kg⁻¹ in January, whereas organic Zn concentrations in DS reached maxima of 47.3 ± 19.9 mg kg⁻¹ in August 1995. Zinc in the reducible phase of SPM reached a maximum of 62.6 ± 16.6 mg kg⁻¹ in March, whereas reducible Zn concentrations in DS were significantly greater in July and August and reached maxima of 18.5 ± 2.5 and 18.5 ± 1.6 mg kg⁻¹, respectively.

3.10. Trace metal partitioning; proportions

Two-way ANOVA indicated that the proportion of trace metal partitioned among the 3 phases was dependent on month for Cu, Pb and Zn, on sediment type for ERCu and organically bound Cu, and ERZn and

Table 4

Two-way ANOVA for the partitioning of the trace metals among the 3 phases. ER: Easily reducible metal, R: reducible metal, O: organically bound metal (*: significant at $P < 0.05$. ns: not significant. –: no comparison possible)

Phase	Copper			Lead			Zinc		
	ER	R	O	ER	R	O	ER	R	O
Month	*	*	*	*	*	–	*	*	*
Type	*	ns	*	ns	ns	–	*	*	ns
M*T ^a	ns	ns	ns	*	ns	–	ns	ns	ns

^a M * T = month * type..

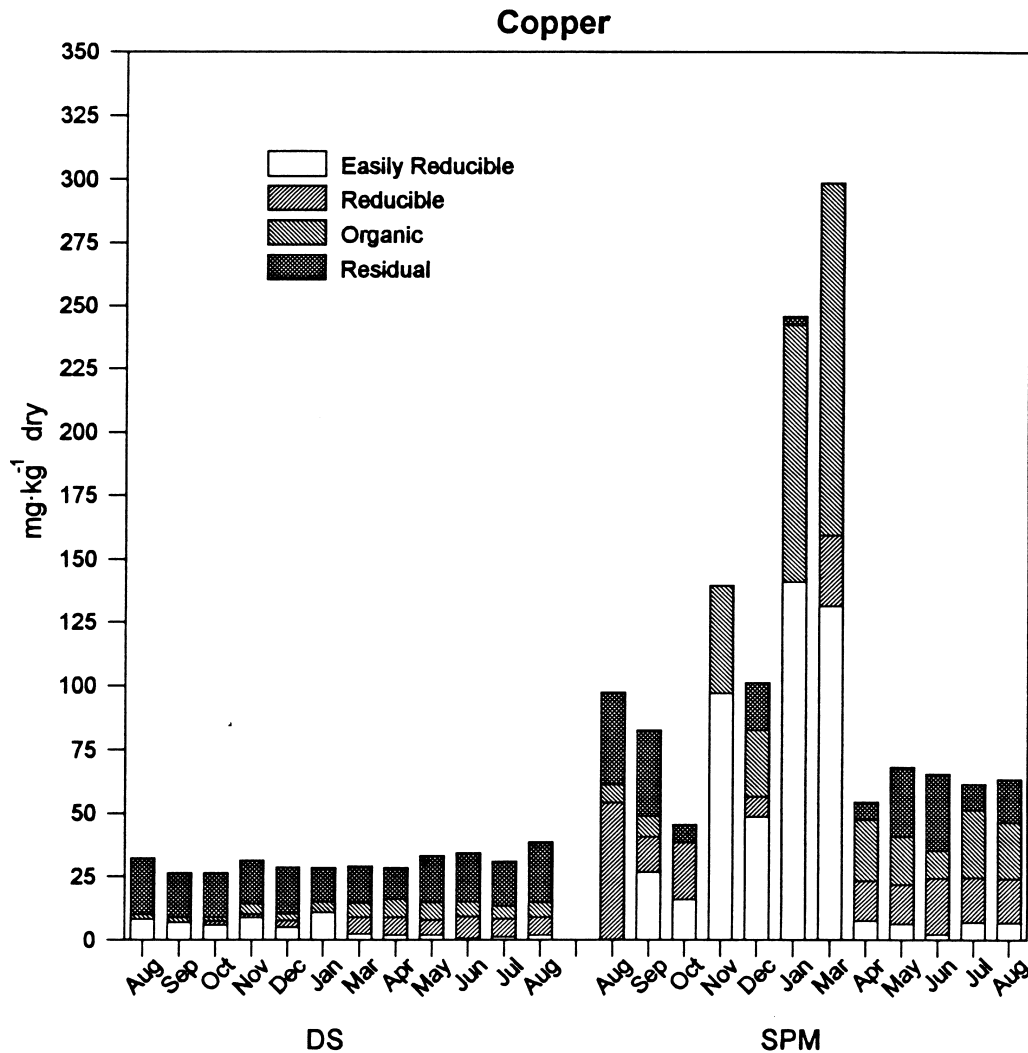


Fig. 12. Concentrations of Cu partitioned among the easily reducible, reducible, organic and residual phases of SPM and DS versus month for the Fraser River Estuary. Values are means \pm 1 S.D.; $n = 9$. In general, coefficients of variation for each of the values are less than 15%.

organically bound Zn, and on the interaction between month and sediment type for ERPb only (Table 4; Fig. 15a–c for Cu, Pb and Zn, respectively).

3.10.1. Copper

SPM contained generally greater proportions of ERCu, and SPM sampled during the winter months of October–March contained greater proportions of ERCu as compared to the summer months. DS followed the same trend as ERCu in the SPM, although a smaller proportion of the overall Cu recovered from DS was as ERCu. The proportion of Cu partitioned onto reducible phases was not significantly different between SPM and DS (Fig. 15a, Table 4). However,

the proportion of reducible Cu (RCu) in both SPM and DS was significantly different among months with winter and summer months containing greater and lesser proportions of RCu, respectively (Fig. 15a). The proportion of Cu in the organic phase was significantly different among months for SPM but not for DS. The proportion of organic Cu in SPM was significantly greater than DS for the months of August, January, July, March and May (Table 4). A major difference in Cu partitioning between the two sediment types was that the majority of Cu in SPM occurred either as ER, R or associated with organic matter (with the month of May and June being the exception). By contrast, on average only up to 50% of the Cu in DS (all months)

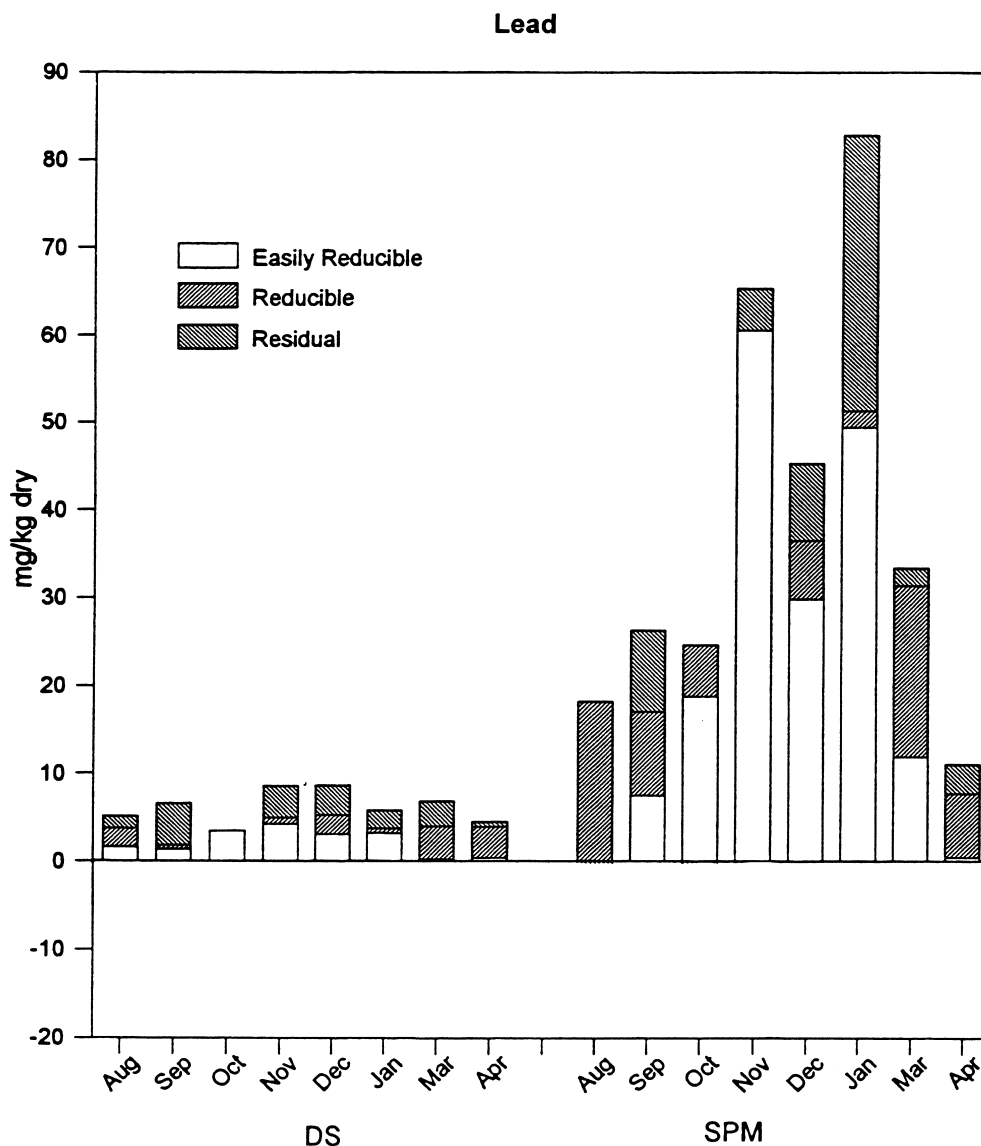


Fig. 13. As in Fig. 12 but for Pb.

occurred as easily reducible or reducible Cu, the remaining being present in the residual fraction (Fig. 15a).

3.10.2. Lead

Lead was not detected in the organic phase, so comparisons among the proportion of metal recovered from each phase could only be compared for easily reducible (ERPb), and reducible fractions (RPb) (Fig. 15b). The two-way ANOVA with sediment type and month as the two factors indicated that the proportion of Pb partitioned into the ER and R components was independent of sediment type but dependent on month. ERPb was dependent on the interaction

between month and sediment type (Table 4). In general the proportion of ERPb in both DS and SPM was greatest during the winter months (from October through to March) as compared to the summer months. During the summer, the majority of Pb was associated with the reducible sediment component. Although the proportion of residual Pb varied from month to month there was a seasonal shift of Pb from the easily reducible fraction to the reducible fraction (i.e. when amounts of ERPb increased, amounts of RPb decreased and vice versa).

3.10.3. Zinc

Two-way ANOVA indicated that the proportions of

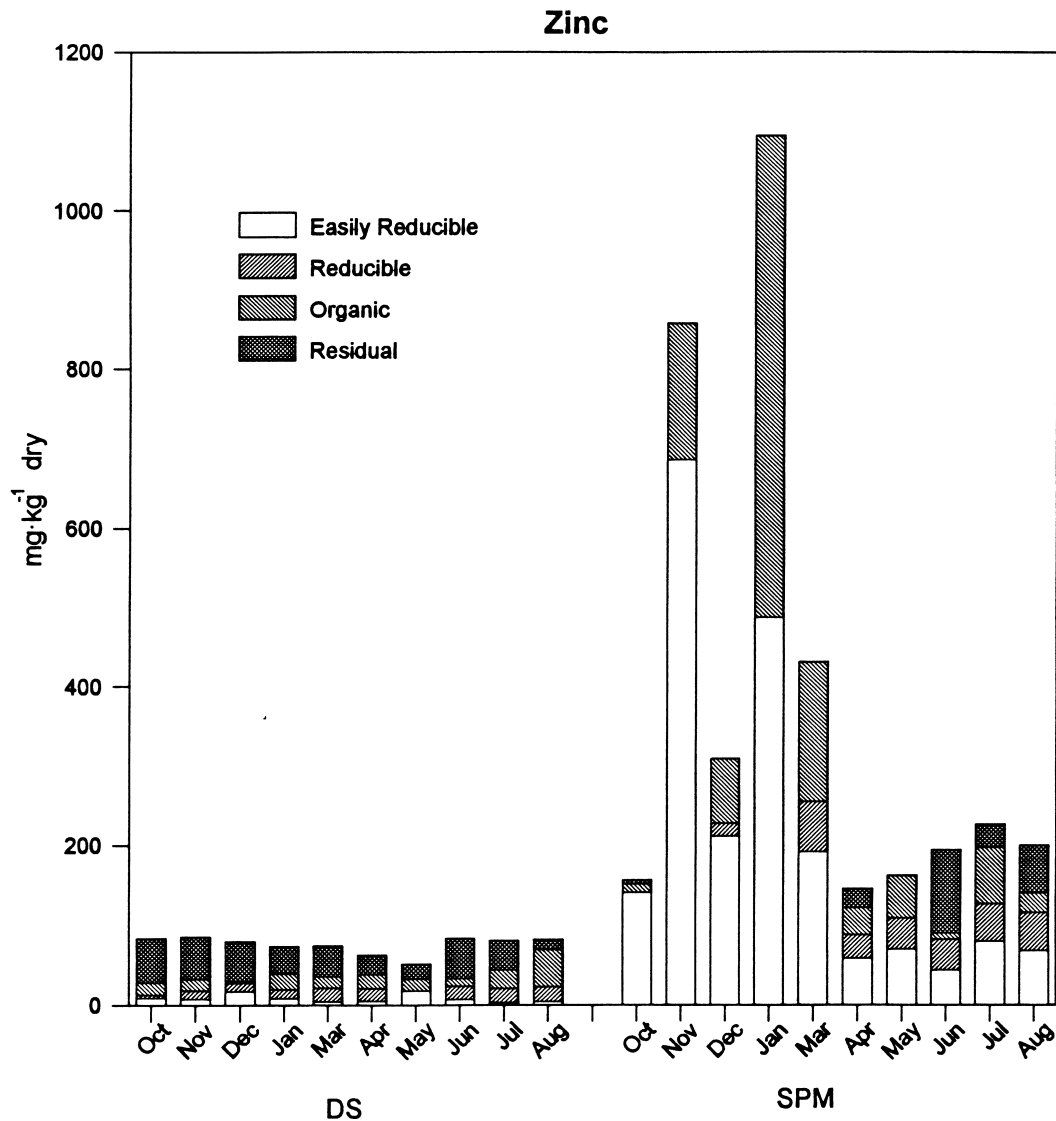


Fig. 14. As in Fig. 12 but for Zn.

Zn partitioned into the easily reducible (ERZn) and reducible (RZn) components of sediment were dependent on month and type of sediment, but were independent of any interaction term (Table 4). In contrast, Zn in the organic phase, was significantly different among months but was independent of sediment type. Thus the same proportion of Zn partitioned into the organic components of sediment for both SPM and DS and this partitioning was dependent on month (Table 4). The proportion of ERZn was significantly greater in SPM than DS in all months but May. The proportion of RZn was significantly greater in DS than SPM in April and January; no other significant differences among months occurred (Fig. 15c).

4. Discussion

4.1. Physio-chemical

Overall, the physico-chemical characteristics of the study area were dominated by seasonal influences with expected seasonal trends (e.g. the seasonal effect of discharge). A strong tidal influence on physico-chemistry was not apparent. The higher salinity recordings noted at the downstream site during November and in January (for the site closest to the mouth of the estuary), coincided with the periods of lowest river discharge. During this period, the lower reaches of the estuary (most notably the “downstream” site closest to the

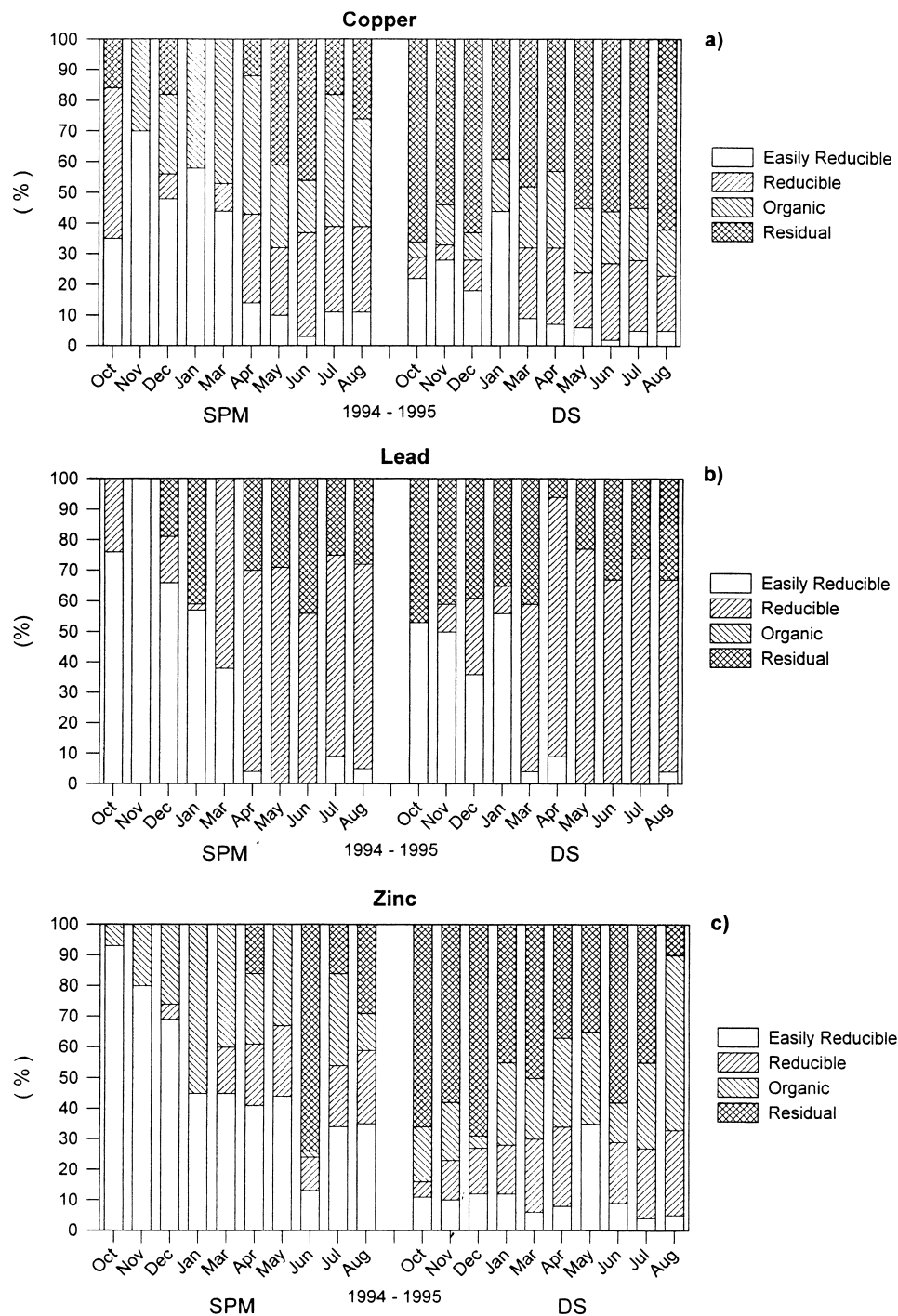


Fig. 15. Proportion of (a) Cu, (b) Pb and (c) Zn partitioned into the 3 sediment components of SPM and DS versus month for the Fraser River Estuary.

ocean), experienced the greatest marine influences. Maxima in pH were observed in the months of May and June concurrent with the spring freshet and were likely due to the increased buffering capacity of river-dominated waters under conditions of high-flow.

4.2. SPM concentration

Highest SPM concentrations were observed under conditions of greatest discharge. Warren and Zimmerman (1994a) also found the concentration of SPM to vary directly with river discharge. SPM concentrations were below 10 mg L^{-1} (wet weight) from November 1994 to March 1995, rising with discharge to $20\text{--}70 \text{ mg L}^{-1}$ from June to August with the greatest SPM concentrations corresponding to highest river flow (70 mg L^{-1} at the midstream site, June 1995).

4.3. Particle size

The major size difference between the two sediment types was that DS comprised 10 to 50% sand ($>62.5 \mu\text{m}$), whereas SPM was primarily composed of particles $<40 \mu\text{m}$ in diameter. As the volume of SPM was highly correlated with flow, a seasonal variation in SPM particle size with flow might be expected because larger particles could be suspended by stronger flows. However, there was little difference in particle size between the months of May and August (discharges of 5500 and $3500 \text{ m}^3\text{s}^{-1}$, respectively). This is consistent with Warren and Zimmerman (1994a), who found that particle size distribution was independent of the SPM concentration and discharge, with the majority of the SPM in the Don River (Toronto, Canada) being $<10 \mu\text{m}$ in diameter. Conversely, Duinker et al. (1985) found a maximum grain size of $8.5\text{--}10.7 \mu\text{m}$ at high SPM concentrations, and a smaller maximum grain size ($4.3\text{--}5.2 \mu\text{m}$) at lower SPM concentrations. Particle sizes were particularly fine during slack water and were smaller than the mean SPM particle sizes of $10.5\text{--}12.5 \mu\text{m}$ found in the present study. However, particle sizing was only possible when high flows made sufficient material available. Hence, it was likely that SPM particle sizes were only measured when a higher proportion of larger particles were present. It has been suggested that the $<62.5 \mu\text{m}$ fraction is sufficiently fine that almost any flow will result in suspension. This fraction is therefore supply limited, while the $\geq 62.5 \mu\text{m}$ fraction is flow limited (Knighton, 1984). Indeed, in this study, only a very small percentage of particles were greater than $40 \mu\text{m}$. Given this observation and the fact that this sediment represents material of larger particle size relative to other times in the season, it is likely that the SPM was comprised of material almost exclusively $<62.5 \mu\text{m}$.

5. Geochemical matrix; organic content, reducible iron (RFe) and easily reducible manganese (ERMn)

5.1. Organic content

The organic matter content of SPM was significantly greater than DS with a distinct seasonality occurring for SPM. Observed differences in the organic content of SPM versus DS may in part be related to the particle size differences that occurred between the two types of sediment. Concentrations of aquatic organic matter display a strong positive relationship with decreasing particle size (Forstner and Wittman, 1981; Salomons and Forstner, 1984; Horowitz and Elrick, 1987). Douglas et al. (1993) found a systematic increase in organic C with decreasing particle size, down to the colloidal fraction. In addition, smaller material is believed to be richer in bacteria (Rao et al., 1993), the specific gravity (suspendibility) of organic particles is low, and the terrigenous/mudflat supply of organic material to SPM may be greater than to DS.

The observed seasonality in the organic content of SPM (i.e. highest in low flow conditions), is consistent with previous findings (e.g. Degens and Ittekkot, 1985; Duinker et al., 1985). A possible reason for the winter maxima in organic matter could in part be related to the contribution of sewage from the Annacis sewage treatment plant (Fig. 1). However, total contributions of organic matter from the plant to amounts of determined SPM organic content were estimated at only 1.12% and 0.6% under conditions of low and high flow, respectively, which in itself does not explain the close to 5-fold difference in SPM concentrations of organic matter between winter and summer months.

Ongley et al. (1982), attributed seasonal shifts in the organic content of SPM to; (1) the dilution of spring sediments with mineral material from active shore-line erosion, (low concentrations) and (2) summer instream production (high concentrations). However, in the current study, a dilution of the SPM with more mineral like material was not reflected by a concurrent increase in SPM reducible Fe (oxides of Fe) content (see discussion below). In addition, in contrast to the findings of Ongley et al. (1982), sustained high flows in the Fraser River are associated with continuous summer snow melt. Lower flow rates occur only in the winter, with minimal autochthonous organic matter production occurring within the river throughout the cold winter months. Clearly, further studies to elucidate the mechanisms that result in the seasonal maxima in SPM organic matter concentrations are highly warranted.

5.2. Reducible Fe (Fe oxides)

The reducible Fe (RFe) concentration of SPM was

generally greater than that of DS, especially during low flow conditions (November through April). A seasonal trend in the RFe content of SPM and DS was also present. As with organic matter, reasons for the strong seasonality in RFe concentrations for SPM (and to a lesser extent DS) are not clear, although the seasonality observed in the study has been noted previously (Carpenter et al., 1975). Maxima in RFe in SPM occurred during conditions which would not favor oxide formation; low flow causes minimal shoreline erosion (which could contribute to a more mineral sediment) and cold temperatures would reduce the rate of Fe oxide formation.

Particle size could be an important factor leading to the observed seasonality in SPM concentrations of Fe oxides and organic matter. For example, although not measured during periods of extreme low flow, finer grained particles with higher average surface areas could be transported, with these surfaces scavenging greater amounts of organic matter and oxides of Fe from the water column in the winter as compared to summer months. However, as previously noted, the particle size of SPM was not significantly different between May and August, periods of high and low flow, respectively, whereas concentrations of organic matter were greater in May as compared to August, suggesting the two are independent. As well, concentrations of Mn oxides did not demonstrate a seasonal dependence, which if influenced solely by a seasonally dependent particle size distribution would have been expected to occur.

Wangersky (1986) has noted that organic matter plays an important role in the distribution of Fe in estuaries and serving as a scavenging surface for Fe. Indeed, studies on the geochemistry of lake sediments (Bendell-Young and Harvey, 1992; Tessier et al., 1996) showed the behavior of reducible Fe and organic matter to be closely related. One explanation in part, could be that concentrations of Fe oxides in SPM are dependent on sediment organic content and hence seasonal fluctuations in organic matter could translate into greater amounts of Fe oxides which are scavenged from the water column by organic matter.

Concentrations of RFe in DS recovered from the sediment/water interface within estuarine systems are primarily from two sources: diagenetic processes and deposition from the overlying water column. This is highly relevant to the current study, in that all 3 sampling locations were located in zones of sediment accretion (i.e. sediments are accumulating rather than being eroded and transported to the delta; McLaren and Ren, 1995). Hence, the seasonal pattern of DS RFe content which paralleled the seasonality in SPM RFe concentrations could be the result of the settling of fresh SPM enriched with RFe to the sediment/water interface. That concentrations of RFe are lower in DS

versus SPM suggests that supply from diagenetic processes within this region of the estuary does not exceed that which is supplied from SPM that has settled at the sediment/water interface. It is possible that the supply of RFe from settling SPM (suggested by the similar seasonal pattern in RFe SPM and DS content), in this case, is the primary source of RFe to the sediment/water interface within this portion of the Fraser River estuary.

5.3. Easily reducible Mn (ERMn)

ERMn was generally greater in SPM as compared to DS, and was highly variable among months for both SPM and DS. Higher levels of ERMn in SPM relative to DS could in part be related to particle size differences as noted for organic matter. For example, Kersten and Forstner (1989) noted that Mn oxide concentrations were greatest in the <2 μm size sediment fraction. Manganese is a redox sensitive species, hence, diagenetic processes can be an important source of Mn oxides to the sediment/water interface and could therefore contribute to amounts recovered as ERMn from DS. Low amounts of ERMn recovered from the sediment/water interface suggest, however, that the contribution of Mn oxides from diagenetic processes to ERMn concentrations in DS is minimal in this part of the estuary.

The high variability in concentrations of ERMn in SPM could be related to the many interactions between biota and Mn oxides. Ongley et al. (1982) found that Mn oxide concentrations in summer SPM were similar to Mn concentrations in the dominant algal species. Recent research by Sunda and Kieber (1994) has shown that bacteria will coat themselves in Mn oxides, possibly to assist oxidation of organic material which they could not otherwise use. This implies a complex and intimate relationship between bacteria, Mn oxides and organic matter. In addition, the current use of the gasoline additive MMT (methylcyclopentadienyl Mn tricarbonyl) could contribute to concentrations of ERMn, and represents a possible explanation for the temporal variability in the Mn oxide content of SPM.

5.4. Total trace metal concentrations

The total metal content of SPM was generally greater than in DS, especially during low flow conditions, (i.e. November through to March), when concentrations and differences in concentrations between the two sediment types were greatest for Cu, Pb and Zn.

Several studies have noted high metal concentrations associated with suspended particulate matter relative

to bottom sediments (Ongley et al., 1982; Regnier and Wollast, 1993; Van Alsenoy et al., 1993; Gibbs, 1994; Santiago et al., 1994; Sondi et al., 1994). Sondi et al. (1994) found their highest concentrations of metals (Cd, Cu, Cr, Mn, Pb, Ti and Zn) were always in the SPM. Gibbs (1994) also found higher levels of these metals in near surface than near bottom SPM. Van Alsenoy et al. (1993) noted similar relationships, but metals in the $<63 \mu\text{m}$ size fraction approached those in SPM. However, Cu was an exception and was enriched approximately 25 times in SPM over the $<63 \mu\text{m}$ fraction of DS, and approximately 65 times over the bulk sediment.

Greater total metal concentrations in SPM versus DS could be related to a combination of at least two factors; differences in particle size between the two types of sediment (greater trace metal concentrations associated with the smaller versus larger particle sizes) plus greater concentrations of the major sediment binding phases, organic matter and reducible Fe, in SPM versus DS. Indeed, strong correlations between concentrations of total trace metals in SPM and amounts of reducible Fe recovered from the SPM ($r > 0.8$; $P < 0.0001$ for all 3 metals) suggest that Fe oxides are the primary sorptive phases of the SPM. By contrast, no correlations between total metal and any of the 3 geochemical components occurred for DS.

5.5. Trace metal partitioning

In general, greater concentrations and proportions of Cu, Pb and Zn partitioned into the easily reducible phase of SPM as compared to DS. This was especially apparent for both SPM and DS during the winter months. For Cu (in contrast to Pb and Zn), significantly higher proportions were found associated with the organic phase of SPM relative to DS.

The strong association of Cu with organic matter has been observed by many researchers (Tessier et al., 1980; Luoma and Bryan, 1981; Bendell-Young and Harvey, 1992; Warren and Zimmerman, 1994b). Similarly, numerous researchers have found Zn and Pb to be predominantly associated with the easily reducible and reducible phases (Tessier et al., 1980; Salomons and Forstner, 1984; Sinclair et al., 1989). In the present study, both SPM and DS partitioned Cu in the order organic \geq easily reducible $>$ reducible, Pb as easily reducible $>$ reducible, and Zn as easily reducible $>$ organic $>$ reducible. McKee et al. (1989) also found Cu to partition in the order organic $>$ reducible $>$ easily reducible whereas Zn partitioned as reducible $>$ organic $>$ easily reducible.

A major finding of the trace metal partitioning among the various geochemical phases was that more metal partitioned into the easily reducible fraction of

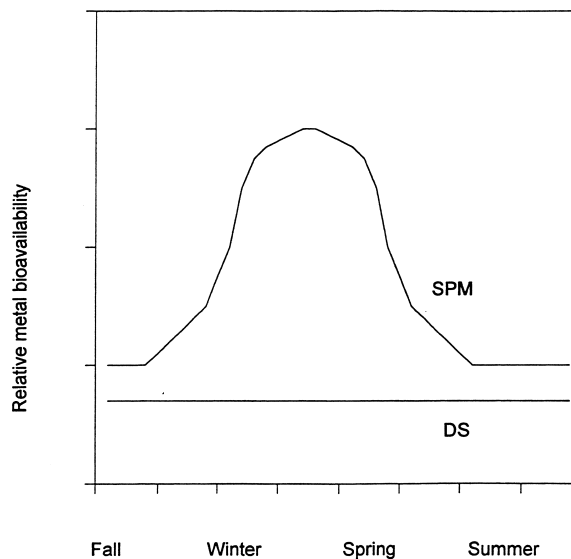


Fig. 16. Theoretical differences between the bioavailability of metal from SPM versus DS as a function of season.

SPM during the winter months as compared to the summer months. The same trend was observed to a lesser degree for Cu and Pb in DS, but not for Zn. The most straightforward explanation would be temperature differences in winter versus summer months (i.e. 4°C versus $16\text{--}18^{\circ}\text{C}$). Metal partitioning onto particulates has been shown to be temperature dependent with partitioning decreasing as temperature decreases (Byrne et al., 1988; Johnson, 1990). Warren and Zimmerman (1994a) noted this effect in their study on metal partitioning in an urban river; during winter months partitioning of Cd, Zn and Cu onto SPM decreased with a concurrent increase in solution concentrations relative to summer months. Similarly, reduced temperatures could lead to metals being less strongly sorbed onto surfaces of binding sites such as Mn and amorphous Fe oxides, and thereby being more readily leachable from the SPM and DS. This would cause greater sediment concentrations of easily reducible metals during periods of low temperature as compared to warmer months.

6. Conclusions

This study has demonstrated that, (1) SPM and DS are geochemically distinct with respect to concentrations of Mn and Fe oxides, organic matter and amounts of trace metals (Cu, Pb and Zn), and (2) a distinct seasonality in the geochemistry of SPM in the Fraser River Estuary which was not observed to the same degree for DS. This seasonality results in signifi-

cant differences in the geochemistry of the two sediment types during winter months (November through April). Specifically, SPM has significantly higher organic content, reducible Fe content (Fe oxide) and total metal concentrations than does DS over this period, with a greater proportion of the associated metal present in an easily reducible form.

The observed seasonality in the geochemistry of SPM relative to DS has important implications for sediment ingesting organisms capable of exploiting both food resources. Metal bioavailability from SPM has the potential to be greater during periods of low flow (i.e. winter months) where a greater proportion of the metal occurs in an easily reducible (bioavailable) form as compared to DS, where seasonality differences are minimal (Fig. 16). Furthermore, organisms that do exploit both food sources tend to filter-feed on SPM during periods of low flow (Miller et al., 1992). Hence, it is possible that facilitative filter-feeders are consuming SPM during a time of year where labile metals are at their greatest.

A major implication of this study is that the bioavailability of metals in SPM has the potential to be highly dynamic, with seasonal fluctuations, such that availability is greatest during the winter months. Correct identification of the routes of metal uptake to facilitative filter-feeders requires that seasonality in SPM geochemistry must be matched with the seasonal feeding behavior of these organisms. Further studies on the feeding behavior of facilitative feeders as a function of season are clearly warranted.

Acknowledgements

This study was supported by an NSERC operating grant to LBY. The field assistance of L. Barjaktarovic, C. Thomas and Z. Arifin is gratefully acknowledged.

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