



Spatial and Temporal Variability of Particulate Trace Metals in Port Jackson Estuary, Australia

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Received 27 June 2000 and accepted in revised form 20 February 2001

Major elements (Al, Ca, Fe and Mn) and trace elements (Cu, Cr, Pb, Zn and Ni) in operationally defined available and total particulate phases have been determined along an axial transect of the Port Jackson Estuary during twelve surveys between 1998 and 1999. Salinity, temperature, pH, dissolved oxygen and suspended particulate material (SPM) were also measured. Temporal and spatial variability were tested by two-factor analysis of variance. Throughout the estuary Zn and Ni exhibited a uniform distribution. It is suggested that the low reactivity of these elements may be a result of the water physicochemistry, low SPM concentrations and long residence time in the Port Jackson Estuary. Anthropogenic sources of Zn and Ni are widespread in the Port Jackson catchment, and also contribute to the spatial distribution observed in the estuary. The distributions of particulate Cu and Pb are significantly affected by anthropogenic inputs, particularly, from the southern embayments in the lower estuary. It is suggested that the increase of Cu and Pb seaward is also related to sorption of these elements on Fe-Mn oxides. Mixing, however, can largely account for the distribution of Cr, which was the only element that presented significant decrease in concentration with increasing salinity. Embayments and tributaries of Port Jackson show distinctive signatures of particulate trace metals (Cu, Pb and Cr), as a result of anthropogenic activities around those embayments. The SPM composition has a significant seasonal variability ($P \leq 0.05$). During spring and summer, the particulate trace metals (Cr, Cu, Pb, Zn and Ni) and major elements (Al and Fe) concentrations are significantly lower than winter. This trend is ascribed to a dilution effect of plankton blooms on SPM composition. © 2001 Academic Press

Keywords: particulate metals; temporal variation; spatial variation; Port Jackson Estuary

Introduction

Estuaries act as a transition zone in which continental material is trapped and through which some of the material is transported to the open sea. The chemical composition and variability of suspended particulate matter (SPM) in estuaries is controlled by a complex interplay of physical and biogeochemical processes. Some of the most important geochemical processes influencing variability are mixing of riverine suspended matter and marine material (Verlaan *et al.*, 1998; Turner *et al.*, 1991), flocculation of colloidal material (Benoit *et al.*, 1994), adsorption and desorption in low salinity zones (Windom *et al.*, 1988; Zwolsman *et al.*, 1997), production of organic matter by phytoplankton (Balls, 1990; Burton, *et al.*, 1994), mobilization of Fe and Mn in reducing sediments (Feely *et al.*, 1986) and resuspension of bottom sediments (Balls *et al.*, 1994). It is not surprising that studies of metal behavior in estuarine waters have documented substantial differences from one estuary to another. Furthermore, few dominant patterns have

emerged, with the exception of removal of Fe from estuarine water of low salinity, as a result of flocculation (Boyle & Edmond, 1977; Windom *et al.*, 1988; Li *et al.*, 1984). Studies on particulate trace metals are usually based on a single, or a small number of surveys. Moreover, the concentration of particulate metals can be variable, both as a result of changing inputs and/or seasonal effects involving biological, geochemical and physical interactions. A common scientific problem in monitoring programs is the absence of consistent, well-prepared sampling design. This deficiency is due mainly to insufficient knowledge of the temporal and spatial variabilities of trace metal concentrations in the area of interest.

The Port Jackson Estuary is regarded as one of the most polluted estuaries in Australia. The estuary has a long history of contamination, which has resulted in extensive areas of polluted sediments, mainly associated with the most industrialized parts of the catchment, in southern embayments and tributaries. Trace metal contamination in the sediments was first reported by Irvine (*pers. comm.*) and later by Birch (1995), Irvine and Birch (1998) and Birch and Taylor

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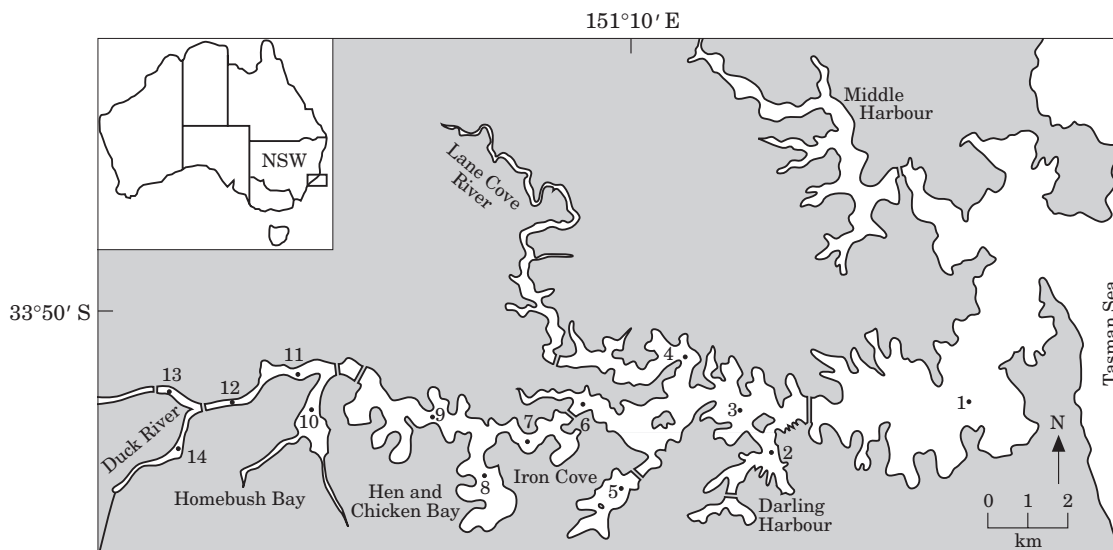


FIGURE 1. Location of sampling stations in the Port Jackson Estuary, Australia.

(1999). Birch and Taylor (1999) showed that storm water discharge via canals is the main point source of contaminants to the estuary and that the embayments of the harbour act as a trap for contaminants. Although SPM is a major carrier by which trace metals are transported to the sea, no studies have been undertaken to understand the geochemistry of particulate trace metals in the Port Jackson Estuary. This work summarizes the composition of SPM, in particular, the particulate trace metal variability in the Port Jackson Estuary. The principal aims of this study were to investigate the spatial and temporal distribution of particulate trace metals along the axis of the Port Jackson Estuary and to identify the processes that control trace metal concentrations in these estuarine waters.

Materials and methods

Study area

The Port Jackson Estuary is a drowned river valley on the south-eastern coastal plain of New South Wales, Australia (Figure 1). The estuary is about 30 km long and drains an area of approximately 500 km². The catchment, mainly composed of Hawkesbury sandstone, is located in the Sydney metropolitan area, and supports the highest population in Australia (~4 500 000) (Zann, 2000). Approximately 90% of the area of the catchment is industrialized, and developments include refineries, breweries, paint industries, concrete and construction manufacturing. The estuary is also very popular for recreational boating

and water sports. The bathymetry of the estuary is irregular, varying from about 3 to 45 m in depth. A number of large, shallow, contaminated bays adjoin the main channel and represent a large reservoir for tidal water. The estuary contains West Central South Pacific water carried southward by the East Australian current and modified within the estuary by minor freshwater inputs (Das, 2000). The typical pattern of freshwater discharge into the Port Jackson Estuary is one of low-flow conditions, punctuated by occasional, brief high flow events. The estuary is generally well mixed, as a result of low freshwater discharge and tidal turbulence (Revelante & Gilmartin, 1978; Sydney Water Board, 1992). Tides are mixed semi-diurnal with a maximum tidal range of 2.1 m and current velocities range between 0.3 and 0.4 m s⁻¹ (Harris *et al.*, 1991). Flushing rates vary considerably along the estuary and a maximum rate of 225 days has been estimated for the estuary (Das, 2000).

Sample collection and pre-treatment

Samples were collected monthly between December 1998 and November 1999 at low slack water, during dry, low flow conditions. Samples collected during January and October were exceptions when moderate flow conditions occurred due to rain periods in the week prior to sampling. Fourteen stations were selected in the Port Jackson Estuary (Figure 1), eight in the main channel and six in tributaries and embayments. Table 1 lists sampling dates together with information on tidal conditions and river discharge volumes.

TABLE 1. Sampling conditions in Port Jackson Estuary, Australia

Date	Tidal range (m)	Days relative to spring (S) tide	Upper Parramatta River discharge ($\text{m}^3 \text{s}^{-1}$)
8 December 1998	1.4	S+4	0.15
29 January 1999	1.5	S-3	0.73
23 February	1.0	S-7	0.22
17 March	1.6	S-1	0.13
27 April	1.1	S-5	0.09
25 May	1.0	S-6	0.25
11 June	1.5	S-4	0.42
28 July	1.5	S	0.32
24 August	1.2	S-3	0.22
21 September	1.1	S-4	0.11
20 October	0.8	S-5	1.7
22 November	1.6	S-1	0.15

Water samples were collected in precleaned polyethylene bottles. The bottles and caps were cleaned by soaking for 24 h in a detergent solution (Pyronex) in a covered tank. They were then rinsed with deionized water (DI; $18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) and soaked in a 10% nitric acid bath for at least 48 h. Finally, the bottles were rinsed three times with DI water and stored in two polyethylene bags. All cleaning operations were carried out in a laminar-flow cabinet and powderless gloves were worn during all procedures.

In the field, the sample bottles were removed from the protective bags and rinsed twice with ambient water. Samples were collected by hand-dipping bottles beneath the water surface. The bottles were capped immediately, sealed inside two polyethylene bags and transported to the laboratory. Temperature, salinity, turbidity, dissolved oxygen and pH profiles were measured at each site with a Water Quality Analyser (Yeo-Kal, model 611). Calibration of sensors was performed before every survey.

In the laboratory, samples were filtered through $0.45 \mu\text{m}$ Millipore (cellulose) filters. Filters were cleaned by soaking in a teflon jar filled with 10% HNO_3 for 5 days, then rinsed with DI water. Filters were dried to a constant weight at room temperature in a laminar flow hood, weighed and stored wet in DI water until being loaded onto filter holders. The filters for SPM determinations were rinsed with 20 ml of DI water to remove salt, dried and subsequently reweighed to obtain the mass of SPM.

Chemical analysis

Filters and retained SPM (0.02–0.05 g) were leached at room temperature for 16 h with 7 ml of 0.05 M

hydroxylamine hydrochloride in 25% acetic acid (v/v) (Tessier *et al.*, 1979). This leach gives an operational measure of metals associated with the particle-bound Fe-Mn oxide coatings, which are potentially available to participate in short-term, biogeochemical reactions. This fraction is referred to as 'available particulate metals'. Although this technique was originally developed for the separation of Fe and Mn oxide phases in pelagic sediments, it has been successfully applied to studies of estuarine suspended solids (Titley *et al.*, 1987; Comber *et al.*, 1995; Turner, 1999). A microwave assisted total digestion of SPM samples was performed with 0.1 ml of HF, 3 ml of HNO_3 and 5 ml of DI water in closed vessels (Method 3051; USEPA). The total digestion was only applied to samples from one month, chosen at random, per season. Copper, Cr, Zn, Pb and Ni were analysed by ICP-MS and Fe, Al, Mn and Ca analysed by ICP-AES.

The precision and accuracy of the analytical technique were assessed by analysis of an International Reference Material, MESS-2 (National Research Council of Canada) with each batch of samples. Because of the small size of the SPM samples (0.02–0.05 g), sub-samples of 0.01 to 0.06 g of MESS-2 were analysed in addition to larger sub-samples of 0.25 to 0.35 g. Since the uncertainties of certified MESS-2 values are given for sub-samples of 0.25 g, or greater, Student's *t*-tests were used to examine differences in the mean metal concentrations measured in small and larger sub-samples of MESS-2. The results indicated significant difference ($P \leq 0.05$) for Zn, Cu and Mn only. The average and standard deviation of the results of the reference material analyses obtained throughout the project are given in Table 2. Average concentration of elements reported here were in agreement within 10% of certified values. The mean recoveries for all elements from spiked samples ranged from 90 to 106% and averaged 98%. Based on replicate analyses of the total and acetic acid digestion, the average precision for duplicate samples was $\pm 8\%$, or better, for all elements. To estimate the precision of the sample collection (i.e. inhomogeneity of water column), in four surveys, independent water samples were collected in triplicate from one site that was selected at random. The percentage of variation ranged from 2.5 to 12% for all elements.

Statistical analysis

Available particulate trace metals, major elements and SPM concentrations were each analysed by two-factor (stations and seasons) analyses of variance (ANOVA) to test the significance of the spatial and temporal variability. The factor 'stations' was random and the

TABLE 2. Quality control results of replicate analyses of metals in standard reference material (MESS-2)

MESS-2	Cr	Cu	Pb	Zn	Ni	Mn	Al (%)	Fe (%)
Certified value (mg kg^{-1})	106	39.3	21.9	172	49.3	365	8.57	4.35
Standard deviation	8	2	1.2	16	1.8	21	0.26	0.22
Obtained mean (mg kg^{-1})*	100	36.8	20.8	150	45.5	344	8.4	4.3
Standard deviation	5.4	0.7	0.4	17	1.3	6.1	0.2	0.1
Average recovery (%)	94	94	95	88	92	94	98	99
Standard deviation	8.7	5.1	5.5	13	4.3	5.7	3.8	5.5
Number of analyses	6	8	8	8	7	6	6	6

*Based on 0.02–0.30 g of MESS-2 and 0.25–0.30 g for Zn, Mn and Cu.

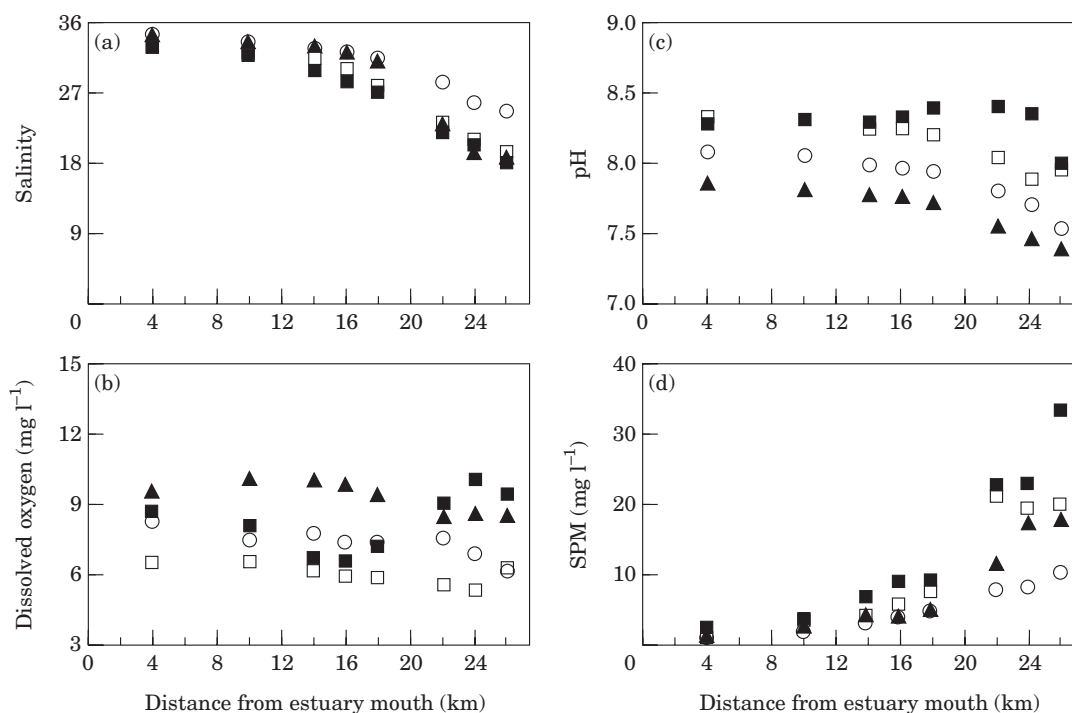


FIGURE 2. Seasonal mean of (a) salinity, (b) dissolved oxygen concentrations (mg l^{-1}), (c) pH and (d) SPM concentrations (mg l^{-1}) in the main channel stations. Standard error bars are not presented for clarity of graphs. Spring (□), Summer (■), Autumn (▲), Winter (○).

factor 'seasons' was fixed and orthogonal. Homogeneity of variances was examined using Cochran's test, and where it was significant, heterogeneity was removed by a $\log_e(x+1)$ transformation. To test differences between seasons, monthly samples collected in each season ($n=3$) were analysed as independent replicates.

Results and discussion

Estuarine major physicochemical variables

Axial transects of estuarine major physicochemical variables, for each season and at each station, are

given in Figure 2. Mean salinity increased gradually from around 18 in the upper estuary to about 35 at the estuary mouth. The minimum salinities (~ 10) were observed in January and October, and are attributable to rain during the week prior to sampling. In these surveys, the upper reach of the estuary was stratified, with less dense surface water (~ 10 salinity) above a more saline bottom layer (~ 20 salinity), progressing to well mixed toward the estuary mouth. However, halobars (not shown) were near vertical through the estuary in all other surveys, indicating that the estuary is generally well mixed and almost entirely saline under low flow conditions. The low salinity zone (i.e.

salinity ≤ 5), where most flocculation and particle scavenging processes occur (e.g. Shiller & Boyle, 1991; Kraepiel *et al.*, 1997; Gustafsson *et al.*, 2000), is not found in the main channel of Port Jackson Estuary under low flow conditions.

The mean water temperature varied from 15.9 ± 0.2 °C in winter to 26.5 ± 1.4 °C in summer. The upper reaches of the estuary were warmer than the estuary mouth during spring and summer and the reverse trend was observed in winter.

The dissolved oxygen profiles showed higher concentration than those previously reported by Irvine (*pers. comm.*), possibly due to reductions in sewage and organic matter inputs over the past 20 years. In general, the dissolved oxygen concentrations increased with increasing salinity and the surface water was saturated in dissolved oxygen. Nevertheless, a temporary decrease in the dissolved oxygen concentration occurred in the upper estuary during spring and winter. Laxton (1998) also observed low dissolved oxygen concentrations (≈ 3 mg l⁻¹), during spring in Upper Parramatta river waters.

An increase in pH was observed during summer. The higher pH was probably associated with photosynthesis during plankton blooms. Filtered materials from summer samples were distinctively greener than filtered material from other surveys. Scanning electron microscopy images (not shown) and visual observation of water samples also indicated the presence of plankton during summer.

No data are available for the annual input of suspended sediments to the estuary. The extended low flow condition together with low SPM concentration (0.5 to 40.5 mg l⁻¹) in the estuary suggests that the supply of sediments is restricted to moderate to high discharge events. Maximum SPM concentrations occurred upstream of Homebush Bay, and decreased seaward by one order of magnitude. This decrease is mainly attributed to the estuarine mixing and settling of SPM. The highest SPM concentrations observed in the shallow upper reaches of the estuary reflect the resuspension of bottom sediments, with high contents of mud, caused by turbulent fluctuations of the horizontal and vertical components of velocity (Coutts-Smith, *pers. comm.*). A recent investigation of the tidal cycle influences on SPM composition, also showed that, in bottom waters, SPM concentrations undergo cyclical changes due to resuspension of the bottom sediments upstream of Homebush Bay (V. Hatje, *in preparation*). However, the development of a 'turbidity maximum zone' in Port Jackson is very poorly documented. Coutts-Smith (*pers. comm.*) suggests that a 'turbidity maximum' originates from the occurrence of gravitational circulation during large,

infrequent flood events and that turbulent energy is responsible for its maintenance during low flow conditions. While it seems clear that the 'turbidity maximum zone' is linked closely to tidal resuspension, the processes responsible for focusing mud accumulation in the bottom sediments is still uncertain. Summer concentrations of SPM were significantly ($P \leq 0.001$; Table 3) higher than concentrations in spring, autumn and winter, and further, these variations were more pronounced in the 'turbidity maximum zone'. Since the occurrence of high flow events is episodic (aseasonal), these data suggest that seasonal variation in SPM concentrations is more likely to be associated with changes in water temperature and an increase of threshold velocity required to resuspend more cohesive sediments during winter than freshwater discharge. Biological processes, such as primary productivity and algal mats forming on the sediment surface during winter, may also contribute to seasonal variability of SPM (Taylor, *pers. comm.*).

Profiles of major elements: Ca, Al, Fe and Mn

The major element concentrations are plotted as a function of salinity in Figure 3, the results of the ANOVA are shown in Table 3 and the ratio Fe/Mn is shown in Table 4.

Hydrous Fe and Mn oxides are important host phases for trace metal contaminants due to their high adsorptive capacities and low degrees of crystallinity (Chao, 1984). Concentrations of available and total particulate Fe are at maximum in the uppermost estuary, whereas available particulate Mn has significantly higher concentrations in the lower estuary ($P \leq 0.001$; Table 3). Zwolsman and van Eck (1999) and van Alsenoy *et al.* (1989) have found similar distributions of particulate Fe and Mn concentrations in estuaries elsewhere. The particulate Fe and Mn profiles in Port Jackson suggest that the remobilization of bottom sediments by resuspension and bioturbation, in the upper reaches of the estuary may release dissolved Mn and Fe to the water column. Dissolved Fe is rapidly oxidized in the overlying water, producing Fe oxide coatings. Manganese, which is also a redox-sensitive element, is oxidized more slowly than Fe in natural systems (Sung & Morgan, 1980) and is transported further downstream before precipitating in the lower estuary. The diagenetic mobilization of Fe and Mn in estuaries is widely recognized (Sundby *et al.*, 1986; Paulson *et al.*, 1989; Owens *et al.*, 1997) and can be a major source of these elements for Port Jackson estuarine waters. Concentrations of Fe and Mn show significant variability between seasons ($P \leq 0.001$; Table 3). Concentrations of Fe were

TABLE 3. Summary of two-factor analysis of variance of concentrations of available particulate metals and SPM in stations and seasons. Each metal was analysed separately

Source of variation	d.f.	Cr			Pbt			Ni			Cuf†			SPM†		
		MS	F	P	MS	F	P	MS	F	P	MS	F	P	MS	F	P
Stations (St)	7	9682	13.8	***	0.41	5.7	***	3.35	1.4	ns	1.67	17.7	***	8.06	90.6	***
Seasons (Se)	3	4352	14.4	***	0.19	12.0	***	3.90	1.4	ns	1.63	42.5	***	2.82	54.5	***
St × Se	21	302.9	0.4	ns	0.02	0.2	ns	2.79	1.1	ns	0.04	0.4	ns	0.05	0.6	ns
Residual	64	704.3			0.07			2.49	Al		0.09	Mn		0.09		
		Zn			Fe											
Source of variation	d.f.	MS	F	P	MS	F	P	MS	F	P	MS	F	P			
Stations (St)	7	16 178	1.9	ns	1 978 869	3.1	*	85 775	0.7	ns	1 405 381	4.9	***			
Seasons (Se)	3	196 857	19.2	***	7 069 144	20.9	***	1 220 145	9.5	***	2 082 309	14.0	***			
St × Se	21	10 254	1.2	ns	5 127 713	0.5	ns	128 135	1.0	ns	148 263	0.5	ns			
Residual	64	8379			387 362			128 477			288 163					

d.f. = degrees of freedom, MS = mean squares, F = F-ratio test, n = 3, † indicates that data were transformed to $\log_e(x+1)$, ns, indicates no significant differences, * indicates significance at $P \leq 0.05$ and *** indicates significance at $P \leq 0.001$.

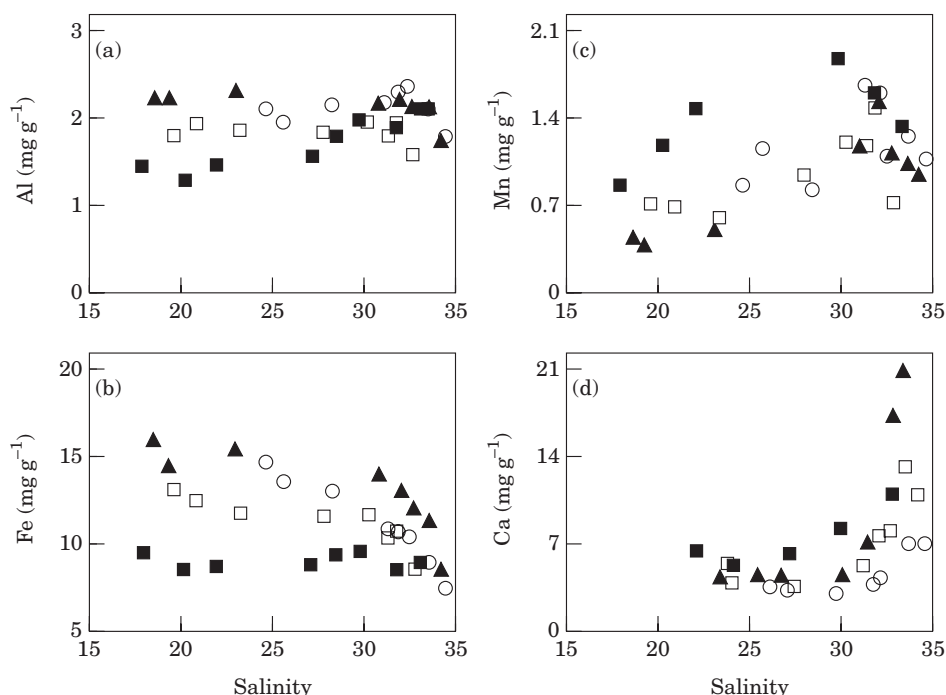


FIGURE 3. Seasonal mean concentrations of available (a) Al, (b) Fe and (c) Mn *vs.* seasonal mean salinity and total concentrations of (d) Ca *vs.* salinity. Spring (\square), Summer (\blacksquare), Autumn (\blacktriangle), Winter (\circ).

TABLE 4. Summary of available concentrations of particulate Fe and Mn for Port Jackson Estuary and other industrialized estuaries for comparison. Seasonal mean \pm one standard error, and range

	Fe mg g^{-1}	Mn mg g^{-1}	Fe/Mn
Summer (n=24)	8.9 ± 0.6 8.5–9.5	1.6 ± 0.1 0.9–2.2	5.7 ± 0.9 4.4–9.9
Autumn (n=24)	13.0 ± 0.7 8.5–15.9	0.9 ± 0.1 0.4–1.5	14.3 ± 1.2 10.4–22.8
Winter (n=24)	13.6 ± 0.8 7.4–14.7	1.1 ± 0.1 0.8–1.7	11.8 ± 1.6 8.8–19.1
Spring (n=24)	11.2 ± 0.6 7.4–14.6	0.9 ± 0.1 0.9–1.3	11.9 ± 0.9 8.8–14.2
Scheldt‡	0.7–3.8	0.4–1.5	0.9–8.2
Weser‡	4.5–7.2	1.3–5.1	1.4–3.8
Forth Estuary†	3.7–6.8	0.3–0.6	9.0–19.2
Mersey Estuary†	2.9–5.9	0.3–1.2	3.8–11.6
Dee Estuary†	1.6–3.4	0.5–1.5	1.8–7.1

†Bed sediments ($<63 \mu\text{m}$), Turner (2000); ‡Turner *et al.* (1991).

significantly higher in winter than summer and spring, whereas Mn had the highest concentrations in summer. High concentrations of particulate Mn during summer results from enhanced oxidation and subsequent precipitation of Mn at higher water temperatures, as suggested by Morris *et al.* (1982),

Keeney-Kennicutt and Presley (1986), Cossa *et al.* (1990) and Turner *et al.* (1991). The seasonal variability of available Fe and Mn, gives an indication of the abundance of each sorbent phase throughout the year. The mean Fe/Mn ratio (Table 4) doubled from summer to winter, as a result of the concomitant decrease of available Mn and increase in available Fe concentrations, and remained in the same order of magnitude during autumn and spring. The results observed in this study are within the range of Fe/Mn ratios estimated for European estuaries (Table 4), which were determined using the same analytical method as this study (i.e. 0.05 M hydroxylamine hydrochloride in 25% acetic acid). Although good agreement was observed between Fe/Mn ratios in this study and in industrialized estuaries elsewhere (Table 4), available Fe and Mn concentrations in the Port Jackson Estuary were, in general, higher than European estuaries. Geology and climate contribute to these differences.

Calcium has been used previously to trace the landward migration of particles of marine origin in estuaries (Salomons & Mook, 1977; Turner *et al.*, 1992) and to calculate the hypothetical mixture of marine and fluvial material (Nolting *et al.*, 1989). Total particulate Ca concentrations decreased from $13.5 \pm 5.2 \text{ mg g}^{-1}$ in the mouth of the estuary to $3.7 \pm 0.5 \text{ mg g}^{-1}$ in the upper reaches. This

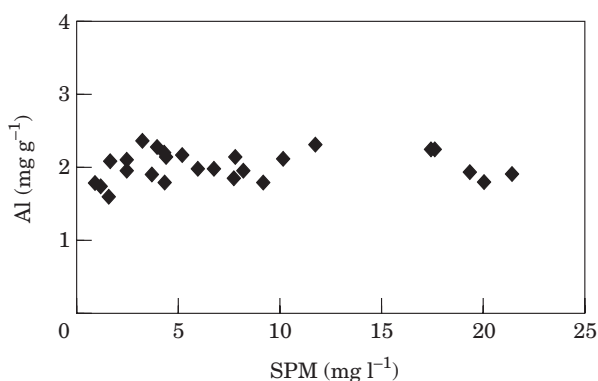


FIGURE 4. Relationship between available particulate Al and SPM concentrations.

distribution of particulate Ca within the Port Jackson Estuary may be explained by the physical mixing of fluvial and marine particles along the small salinity gradient. Because only selected samples were analysed for Ca, there were not enough replicates to test spatial and seasonal variability of this element.

Total and available particulate Al concentrations are more or less independent of salinity during most of the surveys. The absence of a significant ($P > 0.05$; Table 3) spatial gradient in particulate Al concentrations indicates that grain-size effects on the suspended matter is small during low flow conditions. For that reason, the impact of differences in grain size on the trace metal content of SPM is not regarded in this work. This result is confirmed by the uniform distribution of Al with increasing SPM (Figure 4). During plankton blooms in summer, available Al concentrations were significantly lower ($P \leq 0.001$; Table 3) than in winter and total Al concentrations decreased seawards (not shown).

Profiles of trace elements: Cu, Pb, Zn, Ni and Cr

Seasonal mean profiles of trace metal concentrations are plotted as a function of salinity in Figure 5; Fe-normalized metal concentration as a function of SPM is plotted in Figure 6; the results for ANOVA are presented in Table 3; and the percentage of available trace metals relative to the total trace metal concentration are shown in Table 5. From the profiles of trace metal concentrations and ANOVA results, three groups of elements can be distinguished. The first group comprises Cu and Pb, the second group comprises Zn and Ni whereas Cr alone makes up the third group. Spatial distribution trends for all metals were consistent through the sampling period.

It is well known that profiles of particulate trace metal concentrations display intra- and inter-estuarine

variability (Millward, 1995). The commonly observed decline in concentration of particulate metals can be accounted for by the mixing of riverine particles with high metal concentrations, with resuspended bed sediments, or marine particles with lower metal concentrations. Such a mixing process has been suggested to play a dominant role in the Weser and Thames (Turner *et al.*, 1991) and Scheldt estuaries (Zwolsman & van Eck, 1999). Other chemical processes, such as oxidation of resuspended anoxic sediments (Duinker *et al.*, 1982), desorption and differential settling velocities (Millward *et al.*, 1999) can also result in the reduction of metal concentrations.

Most of the particulate trace metals studied, however, displayed patterns different from the expected decrease in trace metal content with increasing salinity. Available Cu and Pb concentrations showed a positive correlation ($P \leq 0.05$) with salinity (Cu, $r = 0.87$; Pb, $r = 0.77$) and a negative correlation ($P \leq 0.05$) with SPM concentrations (Cu, $r = -0.76$; Pb, $r = -0.60$). A study of speciation of particulate Pb (Elbaz-Poulichet *et al.*, 1984) showed that Pb associated with Fe-Mn oxides and organic Pb increase seaward. These authors also showed that about 61% of Pb was associated with Fe-Mn oxides in estuarine SPM samples and 33% with the organic fraction. The available fraction of Pb in the current study, which represents the reactive, or the oxide-bound component of particulate metals, is in good agreement with findings of Elbaz-Poulichet *et al.* (1984) and represents an average of 62% of the total concentration of Pb (Table 5). The increase of Pb and Cu concentrations in Fe-Mn oxide phase is probably the result of sorption of trace metals onto binding sites at the particle surfaces, caused by a rise in pH. It has been demonstrated that a small shift in pH can produce a sharp increase in particulate trace metal concentrations (Hamilton-Taylor *et al.*, 1997; Lead *et al.*, 1999), and further, that Pb and Cu are more strongly bound to oxy-hydroxide surfaces than other trace metals, e.g. Ni and Zn (Forstner, 1987). To better understand the profiles of available Cu and Pb, trace metal concentrations were normalized using particulate Fe concentrations. Iron and Al have been used to normalize trace metal concentrations in estuarine sediments and particulate material (Schropp *et al.*, 1990; Herut & Kress, 1997; Feng *et al.*, 1999). Both elements are abundant in the structural lattices of clay minerals (Salomons & Forstner, 1984) and reflect changes in sediment composition, as well as grain size. Aluminum is often preferable to Fe to normalize trace metal concentrations because Fe is more diagenetically mobile. However, it is this aspect of Fe chemistry that can be of use, because Fe released by redox

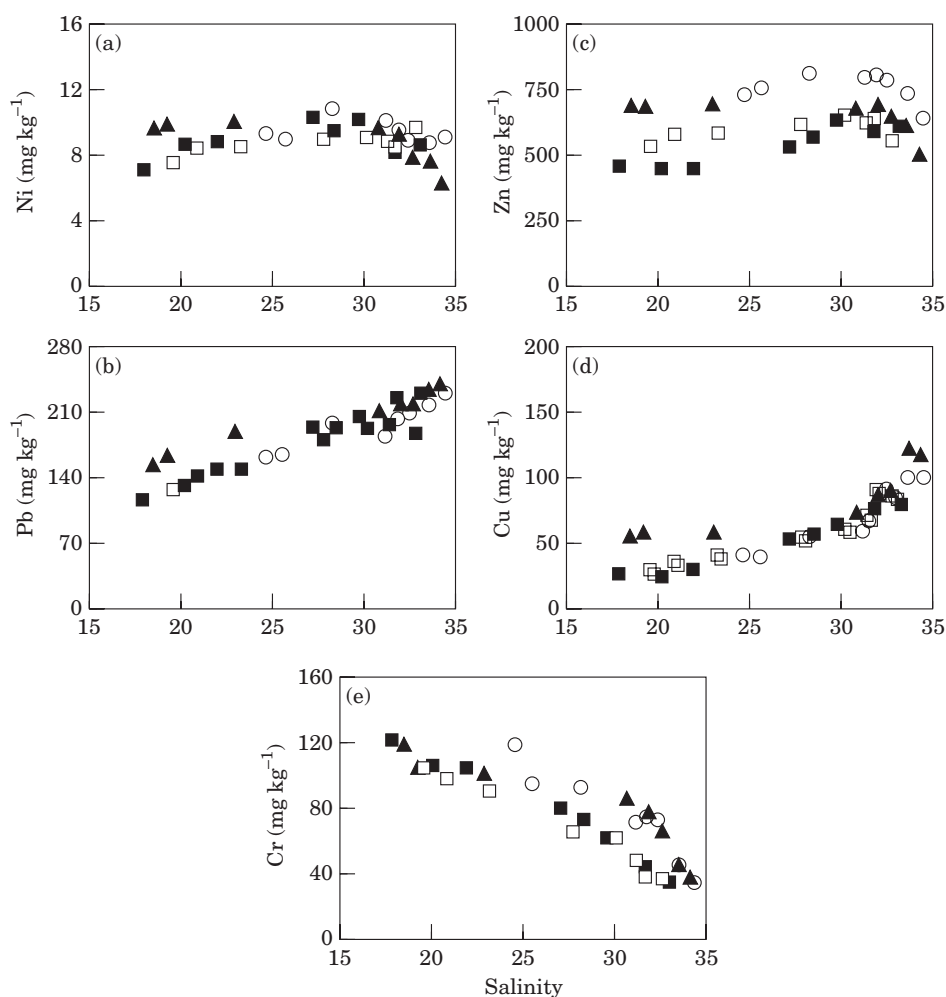


FIGURE 5. Seasonal mean of available particulate trace metal concentrations, (a) Ni, (b) Pb, (c) Zn, (d) Cu and (e) Cr, *vs.* seasonal mean salinity. Spring (□), Summer (■), Autumn (▲), Winter (○).

processes in estuaries can become associated with oxide coatings on particle surfaces (Feng *et al.*, 1999). Even coarse grained, Al-poor particles can have small amounts of Fe in surface coatings (Feng *et al.*, 1999). Moreover, Al concentrations were not measured on all samples, but the good correlation of total and available Fe and Al ($r=0.96$ and $r=0.69$; $P \leq 0.05$, respectively) for the samples in which both elements were measured indicates that Fe may be used to normalize trace metal concentrations. The specific suitability of Fe for normalizing metal concentrations has been demonstrated for the coastal zone (Whalley *et al.*, 1999; Turner & Millward, 2000). Copper/Fe and Pb/Fe ratios exhibit an increase with decreasing particle concentration (Figure 6). It would appear that the distribution of particulate Pb and Cu is not only related to sorption, but also modified by additional inputs of these metals into the lower estuary. Important contributions of Cu and Pb from Iron Cove, Hen

and Chicken Bay and Darling Harbour, which are enriched in these metals, as will be discussed below, are likely to significantly influence the composition of SPM in the lower estuary. Since the SPM concentrations in the lower estuary are low, usually below 5 mg l^{-1} , its composition is more sensitive to anthropogenic inputs.

The concentrations of Zn and Ni, however, are remarkably constant throughout the salinity range, with no significant spatial variability ($P > 0.05$; Table 3) within the estuary. The concentrations of Zn and Ni follow the distribution of Al, which also does not present significant variability between stations. A lack of spatial variability in Zn and Ni concentrations was also reported by Kraepiel *et al.* (1997) in the Gironde Estuary and Carvalho *et al.* (1999) in Paraiba do Sul Estuary. Nickel/Fe, Zn/Fe and also Al/Fe (not shown) ratios were also invariant with increasing SPM, except Zn/Fe ratios in January, which presented a high

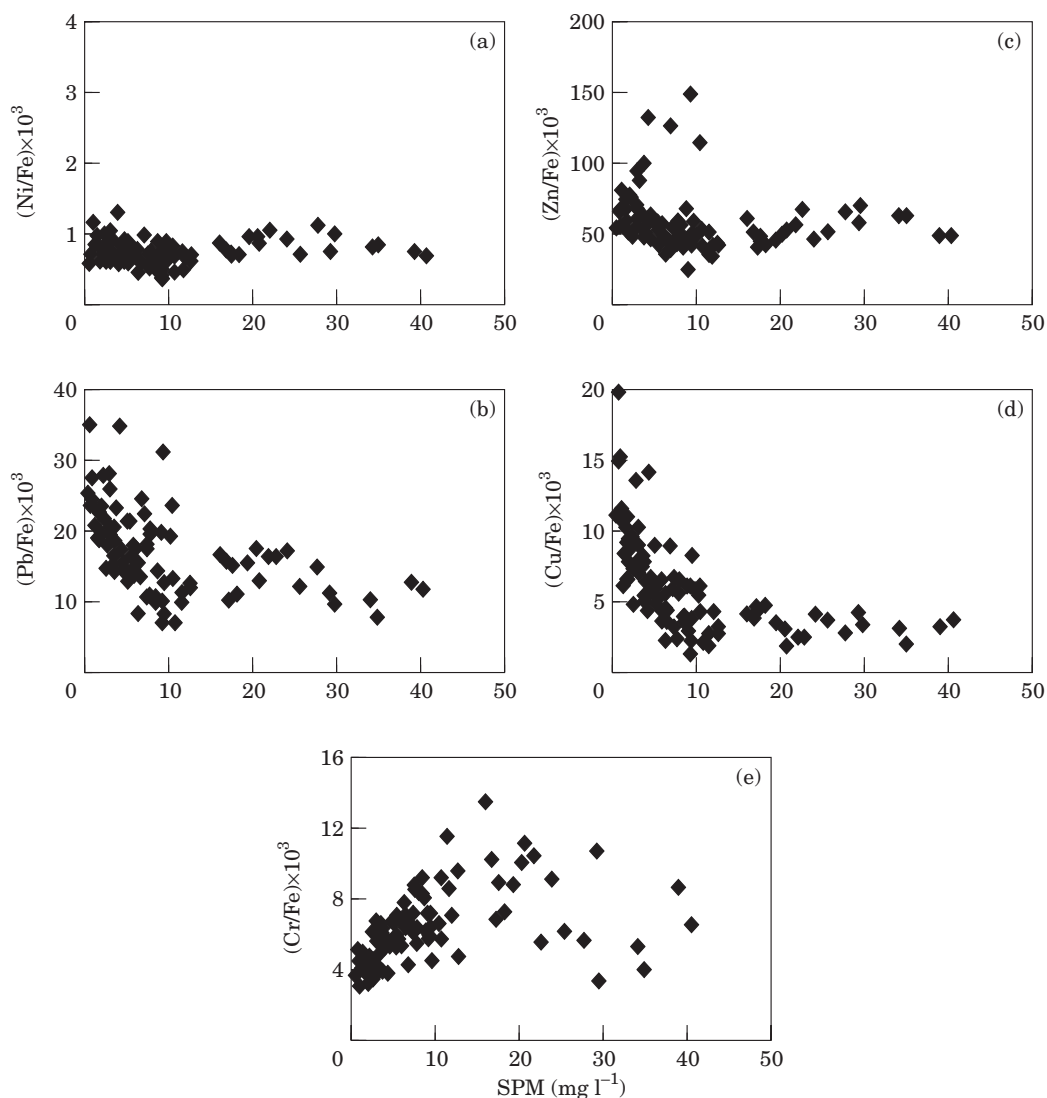


FIGURE 6. Available particulate trace metal/Fe ratios, (a) Ni, (b) Pb, (c) Zn, (d) Cu and (e) Cr, as a function of SPM in the Port Jackson Estuary.

TABLE 5. Percentage of available particulate metal relative to total concentration in Port Jackson Estuary, given as mean (± 1 standard deviation)

n=32	Cr	Cu	Pb	Zn	Ni	Mn	Al	Fe
Mean	31 (7.8)	50 (22)	62 (17)	73 (14)	32 (4.9)	85 (15)	2.4 (0.5)	24 (4.8)

metal/Fe ratio at low SPM concentration. These results may be associated with the slightly higher flow conditions during the January sampling (Table 1). It appears that the behavior of Zn and Ni are associated ($r=0.56$; $P \leq 0.05$) and that anthropogenic sources of both elements are widespread in the estuary. Moreover, the uniform distribution of Zn and Ni through-

out the estuary also reflects the fact that they have a long residence time and the water column is well mixed. Nevertheless, strong gradients in trace metal concentrations in SPM (Barry *et al.*, 1999) and sediments (Birch & Taylor, 1999) were observed in storm water canals and embayments of Port Jackson, mainly because local gradients in physicochemical properties

TABLE 6. Annual mean of available particulate trace metal concentrations (1 standard deviation) and enrichment factors, in italic, in embayments and tributaries of the Port Jackson Estuary and background concentrations in sediments of the Port Jackson Estuary (range). Concentrations in mg kg^{-1}

Element mean (std)	Darling Harbour n=8	Lane Cove n=9	Iron Cove n=10	Hen and Chicken n=10	Homebush Bay n=10	Duck River n=10	Background†
Zn	614.1 (74.8) <i>13.1</i>	566.8 (128.0) <i>12.1</i>	796.5 (198.4) <i>17.0</i>	716.6 (156.6) <i>15.3</i>	600.6 (130.4) <i>12.8</i>	817.1 (364.0) <i>17.4</i>	47 (18–123)
Pb	236.2 (45.6) <i>7.2</i>	183.5 (40.8) <i>5.6</i>	332.1 (75.2) <i>10.1</i>	206.9 (36.0) <i>6.3</i>	180.9 (52.2) <i>5.5</i>	200.3 (78.0) <i>6.1</i>	33 (12–65)
Cu	95.7 (26.9) <i>9.6</i>	83.0 (22.0) <i>8.3</i>	92.2 (29.5) <i>9.2</i>	80.3 (29.6) <i>8.0</i>	44.7 (18.4) <i>4.5</i>	59.1 (26.4) <i>5.9</i>	10 (4–28)
Cr	36.2 (7.6) <i>0.7</i>	29.4 (7.0) <i>0.6</i>	42.2 (15.8) <i>0.8</i>	75.1 (18.6) <i>1.5</i>	85.0 (14.2) <i>1.7</i>	99.1 (43.2) <i>1.9</i>	51 (17–82)
Ni	8.6 (1.4) <i>0.3</i>	8.5 (1.3) <i>0.3</i>	10.3 (2.2) <i>0.4</i>	9.6 (1.6) <i>0.4</i>	11.0 (2.0) <i>0.4</i>	10.2 (3.2) <i>0.4</i>	26 (12–39)

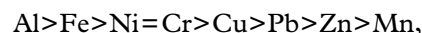
†Total content; Irvine and Birch (1998).

are very steep. It is suggested, therefore, that most of the particle-water interaction (i.e. flocculation, adsorption and complexation) is limited to these canals and headwaters of embayments. The consistent nature of particulate trace metal concentrations (i.e. Zn and Ni) in the main channel, suggest that only a minor fraction of particles are actually reacting with the dissolved phase in the main body of the estuary.

Chromium was the only trace element for which concentrations decreased significantly ($P \leq 0.001$; Table 3, Figure 5) along the estuary. The total and available Cr behaved in a very similar way within the estuary ($r=0.81$, $P \leq 0.05$). Chromium/Fe ratios presented minimum values at very low SPM concentration and exhibit an increase with increasing particle concentration. This can be explained by mixing of river-borne material of high metal concentrations with marine or resuspended estuarine sediments of lower metal content. Physical mixing appears to be the dominant process accounting for Cr distributions. However, sorption and other solid-solution interactions cannot be necessarily dismissed in the explanation of such observations. Chromium is known to associate with Fe-bearing minerals (Nriagu, 1988) and the Cr-Fe strong correlation ($r=0.78$; $P \leq 0.05$) observed in the Port Jackson Estuary suggests that crystalline Fe oxides are partially dissolved by the weak leachate used in this study. Because of the geochemical resistance of naturally occurring Cr (Mayer *et al.*, 1980), excess Cr occurring in more available phases (Table 5) in contaminated environments provides a measure of Cr contamination (Bryan & Langston, 1992). Anthropogenic sources of Cr are situated, mainly, in the upper reaches of the estuary and in Duck River. In contrast to Cr, the other trace

elements studied appear to have anthropogenic sources more widespread in the estuary (Table 6), so the relative importance of particle mixing, in the case of these elements, is masked by direct inputs.

The proportion of available metal to total metal concentration varied from metal to metal. The most to least refractory metals were as follows:



which is similar to that determined by Turner *et al.* (1992) for the Weser estuarine SPM, and by Muller *et al.* (1994) for Clyde estuarine SPM. The high percentage of available metals (e.g. >50% for Cu, Pb and Zn) suggests that a large proportion of the metals are available for biogeochemical processes and that hydrous Fe and Mn oxides are the dominant host phase for Cu, Pb and Zn. Nonetheless, Zn and Cr were the only elements that are significantly correlated ($P \leq 0.05$) with Fe and no significant correlation was observed between trace metals and Mn. It would appear that Fe oxide is the most important sorbent for trace metals in the Port Jackson Estuary. However, since organic matter was not determined as part of this study, its role as a sorbent for trace metals was not evaluated and its effects are not known.

Seasonal variability in trace metal concentrations

Seasonal mean concentrations of Ni were fairly invariant, with no significant differences between seasons ($P > 0.05$; Table 3). However, Cu, Cr, Pb and Zn presented significant differences ($P \leq 0.05$) in estuarine mean concentrations between seasons. For all metals the variance among replicates, i.e. month to

month within each season, was smaller than between seasons. This result indicates that temporal variation at a scale smaller than a season does not play an important role in trace metal distribution in the main channel of the estuary under low flow conditions. However, temporary stratification of the estuary, during high flow conditions, may change the geochemistry of trace metals in the estuary and obscure the temporal pattern observed during low flow. Unfortunately, there is no available data on the geochemistry of trace metals in the estuary under high flow conditions. The short-term variations associated with these events may result in higher variabilities than observed between seasons. The significance and implications of the short-term temporal variations in the concentrations of particulate trace metals in the tributaries entering the Port Jackson Estuary have been shown elsewhere (Hatje *et al.*, 2001).

Concentrations of Cr, Pb, Zn and Cu were significantly higher in winter than in summer and spring. The same result was observed for Al and Fe. Although there were not enough data to test the significance of seasonal variability of Ca, the average concentration during winter was also higher ($7.2 \pm 4.3 \text{ mg g}^{-1}$) than concentrations during summer ($6.0 \pm 2.5 \text{ mg g}^{-1}$). The change in metal concentrations from winter to spring and summer is attributable to variations in the nature of SPM as an impact of the primary production. Since all surveys were realized during low flow discharge (Table 1), there was no variation in hydrological conditions (i.e. river discharge) and/or SPM loads to justify seasonal changes of trace metal concentrations. It is then suggested that during spring and summer there is a dilution of the lithogenous component of SPM by biogenic particles, leading to lower concentration levels of particulate trace metals. This dilution effect of primary production on suspended matter composition has also been reported in other estuaries (Valenta *et al.*, 1986; Windom *et al.*, 1989; Zwolsman & van Eck, 1999).

Trace metals in embayments and tributaries

The embayments and tributaries of the Port Jackson Estuary are predominantly shallow, and the nature of SPM is strongly influenced by resuspension processes during low flow conditions. Taylor (2000) has shown, from data derived from sediment traps, that bottom sediments are continuously recycled into the water column. Because of this continual SPM-sediment interaction, particulate metals reflect concentration levels in surficial bottom sediments. Available metal concentrations in SPM, obtained in the current study, were lower than concentrations in surficial sediments

in all embayments (Irvine & Birch, 1998; Birch & Taylor, 1999). The difference between SPM metal concentrations, determined in this study, and published bottom sediment metal concentrations is partially attributable to the different methods of digestion used in the two studies, i.e. the leachate used in this study has lower recovery compared to hot, concentrated acid digestions employed in studies of bottom sediments. Total digestion was not performed for SPM samples from embayments and tributaries due to small size of samples. Also, the strong decline in trace metal concentrations in bottom sediments away from canals discharging into the upper part of the embayments (Birch & Taylor, 1999) makes it difficult to compare mean concentrations for the whole embayment to SPM concentrations in either total, or available fraction.

Enrichment factors were calculated by dividing the mean concentration of available particulate trace metals from each embayment by the background concentrations of sediments of the Port Jackson Estuary (Table 6). Although the background concentrations were derived from different sampling and analytical approaches (Irvine & Birch, 1998), they serve to estimate the extent to which SPM is enriched or depleted in trace metals. Enrichment factors in SPM were up to 17 for Zn, ranged from 6 to 10 for Pb and from 4 to 10 for Cu. The highest enrichment factors for Cu and Pb were observed in the southern embayments of Port Jackson, in the lower estuary. For Zn, high enrichment factors were found in all embayments and tributaries, indicating that the anthropogenic source of this element is widespread in the estuary. These results agree with the profiles of trace metals in the main channel of the estuary (Figures 5 and 6). Although there is no available data for all the canals entering Port Jackson Estuary, concentrations of particulate metals in those canals that have been measured are generally high. For example, mean particulate concentrations of Cu, Pb and Zn, are 9982 mg kg^{-1} , 3335 mg kg^{-1} , 14790 mg kg^{-1} , respectively, for the canal that drains into Iron Cove (Barry *et al.*, 1999). As a result, this embayment acts as a source of trace metals for the estuary. Urban/industrial stormwater is regarded as the major point source of trace metals for Port Jackson catchment (Birch & Taylor, 1999). Vehicle emissions and antifouling paints are also important sources for Pb, Cu and Zn in the area (Irvine, pers. comm.). Compared to published background levels (Table 6), particulate Ni is not enriched in any of the embayments. Annual mean concentrations were, in fact, half of published background concentrations. Chromium enrichment was low (max. 1.9) and was

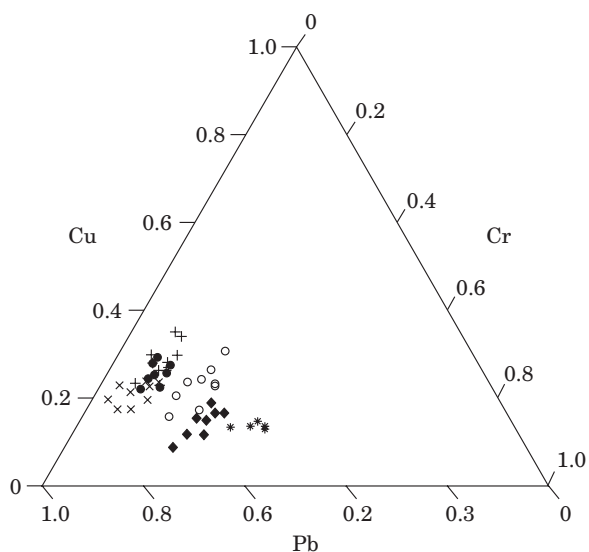


FIGURE 7. Ternary plot of available particulate Cu, Cr and Pb concentrations in the tributaries and embayments of Port Jackson, Australia. Darling Harbour (●), Lane Cove River (+), Iron Cove (×), Hen and Chicken Bay (○), Homebush Bay (◆), Duck River (*).

limited to Duck River and Homebush Bay in the upper estuary. Based on the results of this study, reported background level for estuaries elsewhere, and trace metal concentrations in sediments of Rozelle Bay in the Port Jackson catchment (McCready & Brown, 2001) it is suggested that other published mean background levels for Cr and Ni (Table 6) are overestimated. It is predicted, therefore, that enrichment factors for Cr and Ni are, in fact, up to two fold higher than the value estimated in this study (Table 6).

It is clear from the nature and distribution of enrichment factors and particulate trace metal concentrations obtained in the current investigation, that individual embayments and tributaries exhibit distinct trace metal signatures (Table 6). Nickel and to a lesser extent Zn, were the only elements that were evenly distributed in all studied sites. However, based on a ternary plot of Cu, Cr and Pb concentrations it was possible to distinguish the different embayments and tributaries studied (Figure 7). Suspended particulate matter in Duck River is enriched in Cr and has comparatively low concentrations of Cu, whereas SPM in Homebush Bay has high concentrations of Pb and low Cu concentrations. Similar results were found in Hen and Chicken Bay, with only slightly higher concentration of Cu. Iron Cove is very enriched in Pb, whereas Lane Cove River and Darling Harbour have high Cu and Pb concentrations compared to the other embayments.

Conclusions

An extensive database has been reported, which is believed to be the first comprehensive study of particulate trace metals in the Port Jackson Estuary. Strong contrasts in trace metal distributions were evident. Particulate concentrations of Zn and Ni are relatively unreactive in the main body of the estuary, as a result of the water physicochemistry, low SPM concentrations and long residence time in Port Jackson. Anthropogenic sources of Ni and Zn are widespread in the estuary and also contribute to the uniform distributions of these elements in the estuary. In the case of Cu and Pb, sorption and anthropogenic inputs, especially from the southern embayments in the lower estuary, appear to be the main factors controlling the distribution of these elements in the estuary. The spatial distribution of Cr, however, can be largely accounted for by the mixing of river-borne contaminated suspended particles with relatively uncontaminated marine particles. Such a mixing process was masked by anthropogenic inputs for the other studied trace elements. The abundance of available Fe over Mn (Fe/Mn ratios range from 4 to 22) and the correlations between trace metals and Fe suggest that Fe is the most important oxide phase involved in the sorption of trace metals. Embayments and tributaries have distinctive distributions of Cr, Cu and Pb as a result of anthropogenic inputs to these areas. The SPM composition presents a significant seasonal variability ($P \leq 0.001$) possibly due to plankton blooms during summer and spring, resulting in an increase in biological material at the expense of lithogenic material. In the upper reaches of the estuary, where the SPM concentrations are much higher, the plankton influence in trace metal concentrations is not so clear. The topic of seasonality in the composition of SPM is one worthy of further research, since SPM composition seems to be modified by the presence of plankton during summer and spring, which can also influence its capacity to adsorb trace metals. This means that single surveys for sample collection are representative, at best, of the instantaneous conditions of the estuary. Trend monitoring studies require a comprehensive experimental design to test the significance of temporal and spatial variability in the distribution of trace metals and to unconfound effects of short-term variation.

Acknowledgements

This study was supported by a grant from the Australian Research Council. V. Hatje is sponsored by CNPq-Brazil (200099/96-5). D. Mitchell and

F. Barros are acknowledged for their assistance during field surveys and T. Glasby for statistical advice. We are also very grateful to Ph. Quevauviller and P. L. Brown for helpful comments about the manuscript. The comments of anonymous reviewers were greatly appreciated.

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