Particulate trace metal and major element distributions over consecutive tidal cycles in Port Jackson Estuary, Australia

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Abstract Particulate trace metal (Cu, Cr, Ni, Pb and Zn) and major element (Fe, Mn and Al) concentrations have been determined following intensive sampling over two consecutive spring tidal cycles in the 'turbidity maximum zone' (TMZ) of the Port Jackson estuary, Australia. Salinity, temperature, pH, dissolved oxygen, suspended particulate matter (SPM) and chlorophyll a were also determined. A three-factor analysis of variance was used to test temporal variability in concentrations of particulate trace metals and major elements as a result of tidal oscillation. Estuarine master variables, such as temperature and pH, varied within a narrow range; nevertheless, the tidal signal was clear for surface and bottom waters. In surface water, no variance was detected in SPM concentrations between consecutive tidal cycles or between tidal stages (i.e. flood, ebb and slack water). In bottom water, however, SPM concentrations were significantly higher ($P \leq 0.05$) at flood tide than at slack high water and ebb tide. Concentrations of particulate trace metals and major elements in surface water do not display significant variability between tidal cycles or stages. Nevertheless, differences within each tidal stage were significant ($P \leq 0.05$) for all elements. In bottom water, only particulate Fe and Al exhibited significant differences ($P \leq 0.05$) between tidal cycles, whereas particulate Ni was the only trace element that presented significant differences ($P \leq 0.05$) between tidal stages, following the distribution of SPM, with highest concentrations at flood tide. Among the metals studied, significant variation was found at all three temporal scales examined (i.e. from hours to consecutive tidal cycles), although the patterns of variation were different for each metal. The semi-diurnal fluctuation of SPM and particulate trace metal concentrations during spring tides is interpreted as a resuspension–deposition cycle caused by cyclical oscillations of bottom currents. The results are discussed in the context of the implications of tidal cycle influence on the geochemistry and cycling of particulate trace metals in the Port Jackson estuary.

Keywords Particulate trace metals · Port Jackson estuary · Resuspension · Tidal cycle

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Introduction

The biogeochemistry of estuaries is strongly influenced by temporally variable events occurring at their riverine and marine end members, as well as those impinging on the estuarine water column and sediments. Estuarine responses to temporal variability are complex and often difficult to understand. Nevertheless, a number of observations and insights have allowed identification of some of the important time scales and associated mechanisms of temporal variability, which may apply to a number of estuaries. It has been shown that over the long term, estuarine bed sediments act as a net trap for sediments and associated trace metals from land-based sources (Mulholland and Olsen 1992; Duursma 1995). However, over the short term, ebb advection of freshwater and saltwater intrusion during flood tides dramatically influence the master variables of the water column, such as suspended particulate matter and redox potential (Harbison 1986; Montani et al. 1998), and bottom sediment dynamics (Vale et al. 1993). The extent of such variations will vary greatly depending on spring and neap tide state, or tidal amplitude (Allen et al. 1980; Castaing and Allen 1981; Uncles and Stephens 1996).

The importance of variations in particulate trace metal concentrations on time scales smaller than seasons has been somewhat neglected. This consideration is true for estuaries in which the semi-diurnal tidal ranges, fortnightly tidal variations and freshwater discharge are

relatively low (e.g. Port Jackson estuary). For these estuaries, very small-scale temporal variations may be critically relevant, and they potentially represent an important source of confusion in the identification of temporal patterns. Such problems of confounding results can be overcome by the use of hierarchical replicated sampling design (Underwood 1997). Using such a design, the contribution of variances of each temporal scale can be estimated over the total variance, and the significance of the variation at the scales of interest can be tested against smaller-scale variations.

Estuarine sediment dynamics during a tidal cycle embrace particle resuspension, differential settling, transport of grains and particle–water interactions, i.e. precipitation, flocculation, desorption and adsorption (Turner et al. 1994). Processes that also contribute to sediment resuspension and redistribution in estuarine systems are driven by river flow, shear stresses imposed by wind–wave action, bioturbation and dredging (Calmano et al. 1994; Jago et al. 1994; Lindsay et al. 1996). Altogether, they give rise to a complexity of internal transport routes for heterogeneously reactive chemical constituents and, consequently, to the development of internal cycling and temporary retention mechanisms (Bale et al. 1985).

The purpose of this study is to test the significance of temporal variability of particulate trace metals over tidal cycles in the 'turbidity maximum zone' of Port Jackson, a well-mixed microtidal estuary. Thus, to gain insight on what role resuspension and chemical associated processes may play in controlling trace metal partitioning and transport. This work complements a series of axial surveys performed in the same estuary, which have produced a description of the spatial and seasonal variability of particulate trace metal and major element distributions (Hatje et al. 2001a).

The anthropogenic sources of trace metals to the Port Jackson estuary and the current state of metal contamination in sediments and SPM are described elsewhere (e.g. Birch 1996; Irvine and Birch 1998; Birch and Taylor 1999; Hatje et al. 2001a, 2001b), and will not be discussed in this paper.

Study area

The Port Jackson estuary (Fig. 1) is a drowned river valley on the south-eastern coastal plain of New South Wales, Australia. It drains an area of approximately 500 km^2, has a maximum width of 3 km and the axial distance from the weir (Upper Parramatta River) to the mouth (Tasman Sea) is about 30 km. The estuary has a narrow winding channel and irregular bathymetry, varying from 3 to 45 m in depth. A number of large, shallow bays adjoin the main channel and represent a large reservoir for tidal water. Tides are mixed, semi-diurnal with a maximum tidal range of 2 m and intertidal mud flats are exposed in the headwaters of embayments and the upper reaches of the estuary. Current velocities in the main channel range between 0.3 and 0.4 m s^{-1} (Harris et al. 1991). Freshwater discharge into the estuary is modest and punctuated by aseasonal, short-lived, high-flow events. Under low-flow conditions the estuary is vertically well mixed, and almost entirely saline (Hatje et al. 2001a). Flushing rates vary considerably along the estuary, and a maximum rate of 225 days has been estimated for the estuary (Das et al. 2000). The bottom sediment in the upper estuary and off-channel embayments consists of muds (>95% mud) and a sandy (<1% mud) tidal delta occupies the estuary mouth (Birch and Taylor 1999). Details of circulation within the estuary are not well known and development of the turbidity maximum zone in the upper reaches of Port Jackson is poorly documented.

Methods

Experimental sampling design

An anchor station in the upper reaches of Port Jackson estuary (Fig. 1) was occupied over two consecutive spring tidal cycles on 20–21 January and also 4–5 April 2000. The same sampling design was applied in the two experiments. The sampling design incorporated three temporal scales: tidal cycle, tidal stage (i.e. flood, slack and ebb tide) and hours. During each tidal cycle, in each tidal stage, water
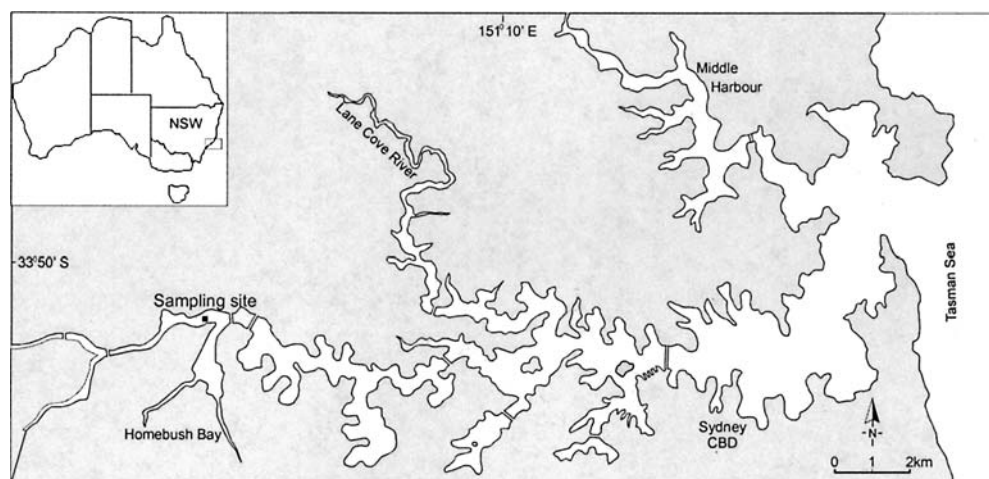

Fig. 1
Map of study area, the Port Jackson estuary, Sydney, Australia

samples were collected on four occasions (hereafter called hours). Two independent replicate samples were collected on each sampling occasion. The total number of samples for each experiment was 48.

Sample collection

Surface water samples were directly collected in pre-cleaned polyethylene bottles or glass bottles (i.e. for chlorophyll a determinations). Bottom water samples were collected using a continuous pumping system deployed at 80 cm above the estuary bed and were stored in precleaned polyethylene bottles. The pumping system was acid washed by circulating HNO_3 solution (5–10%) through the system for 24 h, followed by circulating deionized water (DI; 18 MΩ cm^{-1} resistivity) for 12 h. In the field, ambient water circulated through the system for approximately 3 h before the start of the experiment. Due to operational problems with the pump during the first survey, only 20% of the bottom samples were recovered and interpretation of this data was not attempted. Based on the results of the first experiment, it was decided that only bottom water would be collected in the second experiment. A Falmouth Scientific Acoustic Doppler Velocimeter, and a Multiprobe (6920 YSI) with sensors for pH, salinity, temperature, turbidity and dissolved oxygen (DO) were mounted on a steel pod and placed at 80 cm above the bottom. Temperature, salinity, turbidity, dissolved oxygen saturation and pH profiles were also measured at each sampling time during the first survey with a Water Quality Analyzer (Yeo-Kal, model 611). Calibration of sensors was performed before each survey.

Sample treatment and chemical analysis

In the laboratory, samples were filtered through 0.45-μm 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.

Filter and retained SPM were leached at room temperature for 16 h with 7 ml of 0.05 M hydroxylamine hydrochloride in 25% acetic acid (v/v; Chester and Hughes 1967; Tessier et al. 1979), thereby allowing comparisons with determinations made on previous surveys (Hatje et al. 2001a). 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'. Copper, Cr, Zn, Pb and Ni were analysed by ICP-MS, and Fe, Al and Mn were analysed by ICP-AES. The mean recoveries for all elements from spiked samples ranged from 90 to 106% and averaged 98%. Based on replicate analyses of the acetic acid digestion, the average precision was ±4%, or better, for all elements. Chlorophyll a concentrations were determined by acetone extraction and total organic carbon (TOC) was determined by a combustion-infrared method (APHA 1995).

Statistical analysis

Available particulate trace metals, major elements and SPM concentrations were each analysed by three-factor analyses of variance (ANOVA). Each variable for each experiment was analysed separately. The analyses included three factors. Tidal cycle was the first factor (orthogonal, random with two levels); the second factor was tidal stage (orthogonal, fixed with three levels) and the third factor was hour (nested, random with four levels). Homogeneity of variances was examined using Cochran's test, and where it was significant, heterogeneity was removed by a ln (x+1) transformation. Multiple comparisons among means were performed with the Student–Newman–Keul's (SNK) test.

Results

First experiment, January 2000: surface water

Master variable results for experiments 1 and 2 are shown in Table 1. Maximum salinities of 33.7 were observed at high water, with the minimum of 29.9 occurring at low water. Water temperature and chlorophyll a showed an inverse correlation with salinity ($r=-0.53$ and $r=-0.72$; $P \le 0.05$, respectively). Maximum values of temperature and chlorophyll a were observed at low water, i.e. 26.1 °C and 12.0 μg l^{-1}, respectively, and minimum values at high water, i.e. 24.6 °C and 3.7 μg l^{-1}, respectively. Saturation of DO was at a maximum at high water and minimum saturation (66.6%) was found at low water. Variation of pH over two consecutive semi-diurnal tidal cycles was smaller than 0.2 pH units. No clear pattern was observed for TOC. In the first tidal cycle (Fig. 2), concentrations increased from flood to slack water, and maximum values occurred during ebb tide. During the following cycle, concentrations were minimum at ebb tide and comparable during slack water and flood tide.

Concentrations of SPM (Table 1) were low compared with other microtidal estuaries (Nichols 1993; Niencheski et al. 1994), and were in the same range as those observed previously in the Port Jackson estuary (Hatje et al. 2001a).

Table 1
Mean (standard deviation) of water column master variables for experiment I (January; surface water) and experiment II (April; bottom water)

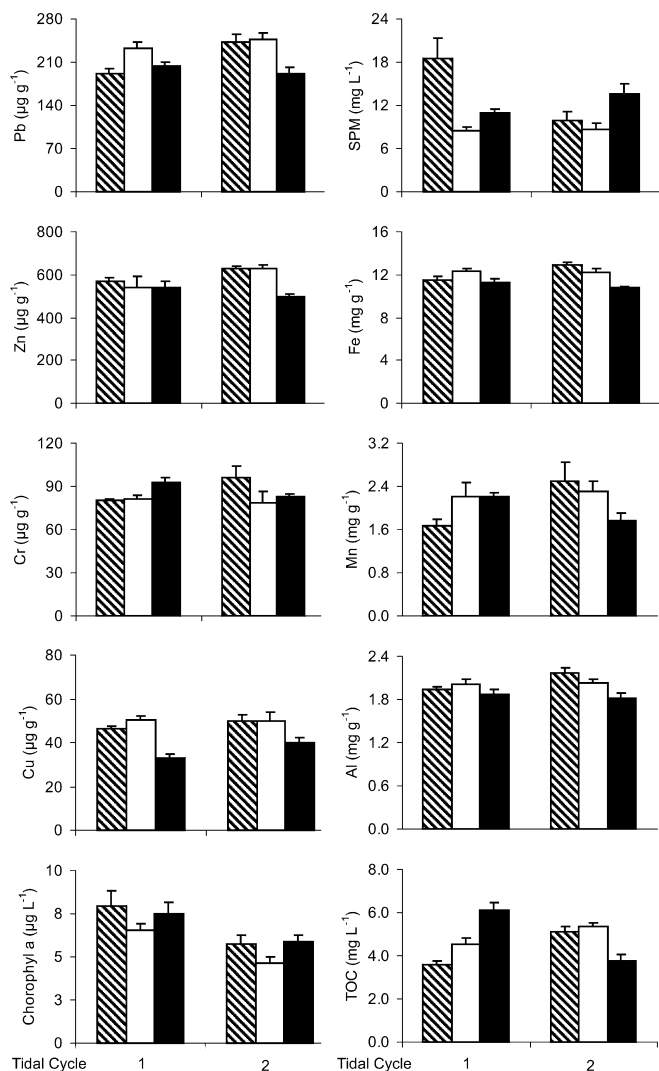| Date	Tidal range (m)	Salinity	pH	Temp. (°C)	Chlorophyll a (μg l^{-1})	TOC (mg l^{-1})	DO (mg l^{-1})	SPM (mg l^{-1})
January	2	32.5 (1.12)	7.72 (0.03)	25.1 (0.60)	6.88 (2.10)	4.54 (1.26)	5.54 (0.62)	11.2 (4.88)
April	1.8	28.0 (1.61)	7.97 (0.05)	22.0 (0.16)	–	–	4.91 (0.36)	16.1 (4.06)

Fig. 2
Mean concentrations (SE) of available particulate trace metals, major elements, TOC, SPM and chlorophyll a on surface waters (experiment I), for two consecutive tidal cycles, during flood (*hatched*), high slack water (*blank*) and ebb tide (*shaded*)

Table 2
Summary of results from three-factor ANOVA tests comparing concentrations of available particulate trace metals, major elements and SPM in surface water (experiment I) over two consecutive tidal cycles (*Ti*), over three tidal stages (*St*) and over 4 h (*Ho*) ($n=2$). $^{n.s.}P>0.05$, $*P \leq 0.05$, $**P \leq 0.01$, $***P \leq 0.001$. Cochran's test was significant only for particulate Zn concentrations

Variable	Tidal cycle (Ti)	Tidal stage (St)	Hour (Ti × St)	Ti × St
SPM	n.s.	n.s.	***	n.s.
Al	n.s.	n.s.	**	n.s.
Mn	n.s.	n.s.	***	n.s.
Fe	n.s.	n.s.	*	n.s.
Cu	n.s.	**	***	n.s.
Cr	n.s.	n.s.	n.s.	n.s.
Pb	n.s.	n.s.	***	n.s.
Zn	n.s.	n.s.	***	n.s.

peaked at flood tide, decreased during high water and attained a minimum at ebb tide. Concentrations of particulate trace metals, in general, tended to be higher at flood than ebb tide and this pattern was consistent for the two tidal cycles.

Second experiment, April 2000: bottom water
Distribution of salinity, temperature, pH, dissolved oxygen (DO) and turbidity at 80 cm above the estuary bed show that these variables undergo cyclical changes during tidal oscillations, and show similar patterns to those found for surface water during the first experiment. The highest values of salinity, DO saturation and pH, i.e. 29.4; 75.9%; 8.03 respectively, are found at high water and the lowest, i.e. 19.8; 55.9%; 7.84 respectively, at low water. Temperature displays the opposite trend to salinity, increasing during ebb tide to values up to 22.4 °C at low water and reaching a minimum of 21.8 °C at high water. Turbidity showed high values at the onset of flood tides (Fig. 3). During each ebb tide, two peaks of turbidity were observed; both peaks occurred before the maximum velocity was attained. Maximum velocities (0.26 m s^{-1}) were observed during flood tide.
The SPM, particulate metal and major element concentrations are shown in Fig. 4. Concentrations of SPM exhibited a maximum value during flood tide and another peak was repeated during ebb tide (Fig. 5). Differences between tidal stages were significant (Table 3). Concentrations of SPM were significantly higher ($P \leq 0.05$) at flood tide than at slack water and ebb tide. No direct relationship between SPM and salinity, or currents was observed.
The particulate metal and major element concentrations were similar to those observed previously (Hatje et al. 2001a) and are in the same range of concentrations reported for bed sediments in the studied area (Irvine and Birch 1998). During the tidal cycle concentrations of particulate trace metals and major elements varied in two ways. Nickel concentrations peaked at flood, in the same way as SPM concentrations, and decreased to a minimum at ebb tide. Maximum concentrations of Cr, Pb, Cu, Zn, Fe and Al were, in general, observed during ebb tide. Among the metals studied, significant variation ($P \leq 0.05$) was
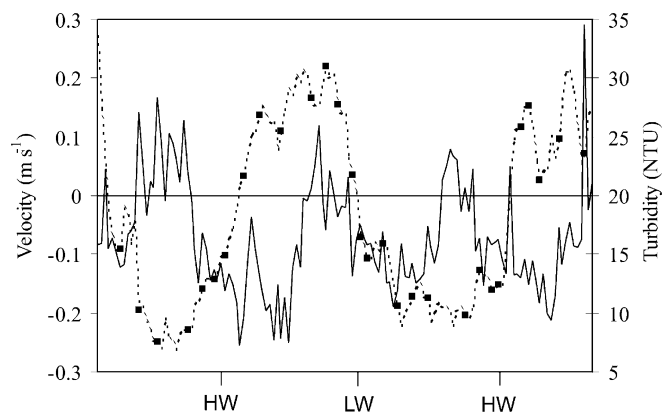
No significant differences were detected in concentrations of SPM (Table 2) between semi-diurnal tidal cycles or between tidal stages. Concentrations of SPM, however, tended to be higher on flood tide than high slack water (Fig. 2) during two consecutive tidal cycles, whereas in the second tidal cycle, SPM concentrations at ebb tended to be higher than at flood tide.
Particulate trace metal and major element concentrations at flood, slack and ebb tides are shown in Fig. 2. In general, both particulate trace metal and major element concentrations did not vary significantly between tidal cycles and stages (Table 2). There were, however, significant differences ($P \leq 0.05$) in concentrations of major elements and trace metals within each tidal stage. Concentrations of Fe, Mn and Al exhibited similar distribution patterns. In the first tidal cycle, concentrations increased during flood, reached a maximum at high water and decreased during ebb tide. In the second tidal cycle, however, concentrations

Fig. 3
Variations of velocity (*dashed line*) and turbidity (*full line*) at 80 cm above the bed. Positive velocities are in ebb direction and negative velocities are in flood direction. *Black squares* indicate the time at which a bottom sample was taken. *HW* indicates high slack water and *LW* indicates low slack water
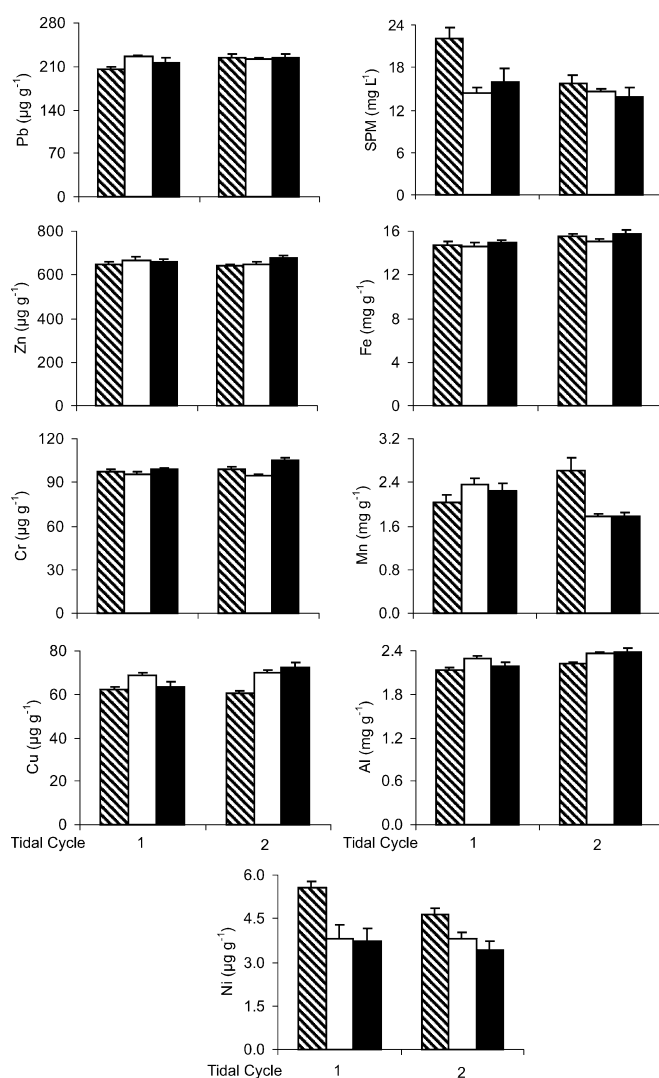

Fig. 4
Mean concentrations (SE) of SPM, available particulate trace metals and major elements on bottom waters (experiment II), for two consecutive tidal cycles, during flood (*hatched*), high slack water (*blank*) and ebb tide (*shaded*)
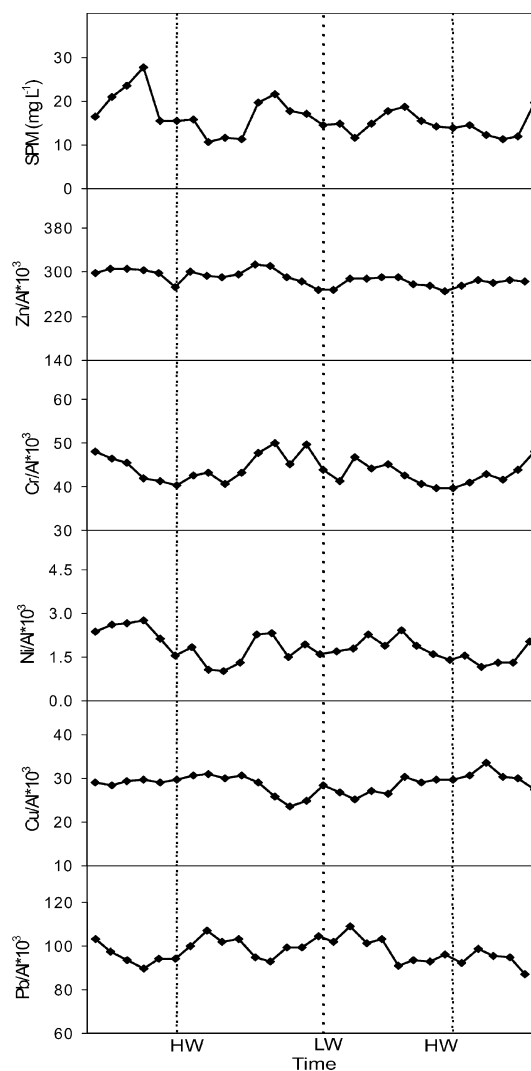

Fig. 5
Variation of available metal/Al ratios during consecutive tidal cycles at bottom water (experiment II) in Port Jackson estuary. *HW* indicates high slack water and *LW* indicates low slack water

Table 3
Summary of results from three-factor ANOVA tests comparing concentrations of available particulate trace metals, major elements and SPM in bottom water (experiment II) over two consecutive tidal cycles (*Ti*), over three tidal stages (*St*) and over 4 h (*Ho*) (*n* = 2). $^{n.s.}P > 0.05$, $*P \leq 0.05$, $**P \leq 0.01$, $***P \leq 0.001$. Cochran's test was significant only for particulate Zn concentrations

Variable	Tidal cycle (Ti)	Tidal stage (St)	Hour (Ti × St)	Ti × St
SPM	n.s.	*	***	n.s.
Al	**	n.s.	*	n.s.
Mn	n.s.	n.s.	***	*
Fe	*	n.s.	**	n.s.
Cu	n.s.	n.s.	***	n.s.
Cr	n.s.	n.s.	**	n.s.
Ni	n.s.	**	**	n.s.
Pb	n.s.	n.s.	***	n.s.
Zn	n.s.	n.s.	n.s.	n.s.

found at all three temporal scales examined, i.e. from hours to consecutive tidal cycles (Table 3).

Discussion

Distribution of SPM concentrations

As suspended sediments and particulate metals are transported by flows, the patterns of sediment behaviour are strongly related to hydrodynamics and oscillations of estuarine master variables during tidal cycles. During this study, the river discharge and SPM concentrations were in the same range observed previously under low flow conditions (Hatje et al. 2001a), and represent the typical dry weather situation in the Port Jackson estuary. Therefore, the effect of river discharge variations when interpreting the distribution patterns can be neglected. The effect of wind-stripping on the SPM distributions can also be disregarded because the meteorological record for the study period reveals no long periods of strong wind. This leaves the tide as the main variable to influence SPM and particulate trace metal distribution patterns.

Concentrations of SPM in bottom water showed a significant variability ($P \leq 0.05$) during the tidal cycle (i.e. between tidal stages), but at the surface no significant variability was found. However, concentrations of SPM in surface water in the first semi-diurnal tidal cycle followed the same behaviour as bottom water. It tended to be highest during flood. In the turbidity maximum zone of Port Jackson, Coutts-Smith (1998) had observed two phases of sediment resuspension during flood and ebb spring tides. However, the turbidity observations of this study indicate a two-phase resuspension process during ebb tide only (Fig. 3). Further, the variation of SPM concentrations during the tidal cycle (Fig. 5) showed evidence of only one peak on each of the flood and ebb tides. The difference between these observations and those of Coutts-Smith (1998) is partly attributable to the distinct sampling designs (i.e. random sampling versus regular sampling intervals) used in each study. However, the position of sample collection, in relation to the channel thalweg, may also have influenced the results.

The lowest SPM concentrations at high slack water, observed at surface and bottom waters, are a common observation in estuaries (Allen et al. 1980; Vale and Sundby 1987). This can be attributed to asymmetry in the current velocity over the tidal cycle, resulting in a long period around high water during which current velocities are low, whereas the corresponding time at low water is comparatively short (Postma 1967). Therefore, at high slack water a longer time is available for settling of suspended material than at low tide. Although little asymmetry can be observed in the current velocities (Fig. 3), Coutts-Smith (1998) observed that, in the upper reaches of the Port Jackson estuary, ebb tide is shorter in duration than flood tide, and this may explain the low SPM concentrations at high slack water. Moreover, Coutts-Smith (1998) has shown that suspended particles that oscillate between suspended and deposited states under the influ-

ence of tidal disturbance, during low flow conditions, are subject to net transport landward. Hence, the upper estuary acts as a zone of accumulation of mobile sediment. It has been reported that a surficial layer (up to 3 cm) of easily resuspended, low density, oxic sediment, termed a hydrous layer, overlies compacted oxic and anoxic bed sediment extensively throughout Port Jackson (Birch and Taylor 1999; Taylor 2000). Resuspension of this surficial hydrous layer during the tidal cycle could quickly exhaust the supply, so that further resuspension would cease. The bed sediment proper, therefore, would contribute little to the resuspended sediment population during a tidal cycle. Coutts-Smith (1998) observed that low SPM concentrations in the turbidity maximum zone coincide with high shear stress, indicating that resuspension was limited by the availability of a suitable source. Comparable source-limitation on tidal resuspension has been observed previously (e.g. Sanford et al. 1991; Jago et al. 1994).

The semi-diurnal variations of SPM concentrations observed during spring tides (Figs. 2 and 4) were very small compared with variations of SPM in other estuaries (Turner et al. 1994; Heruk and Kress 1997; Austen et al. 1999). The range of variation observed in this work and reported previously by Coutts-Smith (1998) were, in fact, smaller than SPM variations at neap tide elsewhere (Gelfenbaum 1983; Vale and Sundby 1987). Based on the magnitude of variations observed in SPM concentrations during spring tides, it is suggested that variations over neap tide will not be statistically significant. Hence, variations in SPM concentrations over semi-diurnal spring tidal cycle may possibly be as large as the overall variation over neap–spring cycle.

Distribution of particulate metal concentrations

Although significant differences ($P \leq 0.05$) were detected in SPM concentrations, the results for particulate trace metals were not as predicted. Effects of the tidal cycle were not clear in the patterns of particulate trace metal distributions at bottom and surface waters, as it was previously observed in meso- and macrotidal estuaries (e.g. Millward et al. 1998). The large variability in concentrations within tidal stages (Tables 2 and 3) is, however, important to note. It is by no means a novel finding, but highlights the importance of the very small-scale temporal variation, the need for adequate temporal replication of experiments and, further, suggests that the generality of results of tide cycle experiments done at a single sampling occasion is not assured.

The data in Figs. 2 and 4 show that particulate metal concentrations over the tidal cycle do not vary in the same magnitude as SPM concentrations. While there is a significant variability in mass of SPM in bottom water due to resuspension, particulate trace metal concentrations did not correlate with that. One explanation is that material resuspended from the hydrous layer is admixing with a permanent population of suspended material (i.e. sediments too small to fall out of suspension during the short period of slack water) without a significant change in SPM composition. This corroborates the fact that tidal cycles

promote a continuous cycling of resuspension of the superficial hydrous layer and, hence, no significant variation was observed in SPM composition. If only a few millimetres of superficial material are resuspended during flood, deposited at slack and resuspended again during ebb, then the sediment has only a few hours to consolidate. Newly deposited sediments are more erodible than undisturbed sediments because several hours are needed for binding of bottom sediments by benthic communities and consolidation of clay minerals (Schoellhamer 1996). Moreover, the continuous resuspension and oxygenation of the sediments is likely to prevent the development of anoxia and hinder the progress of early diagenesis.

To reduce the influence of grain size and mineralogical effects, and to identify possible anomalies in metal concentrations during the tidal cycle, normalization of trace metals to Al was used (Schropp et al. 1990). Metal/Al ratios are presented in Fig. 5. The metal/Al ratios for Cr, Pb, Cu and Zn varied within a narrow range of about 7%, whereas Ni showed a coefficient of variance of 27%. The patterns of trace metal/Al ratios with time show that particulate trace metals peaks are not related to any specific variation of salinity, SPM (except for Ni) and dissolved oxygen concentrations during the tidal cycle. The relatively small changes in metal concentrations can possibly be explained simply by the mixture of the material that is resuspended with the permanently suspended sediment and the marine material transported landward during flood tide.

The oxidative release of metals during resuspension of anoxic bed sediments is likely to be a major source of metals to well-oxygenated overlying waters. Iron and Mn sulfides are usually present in large excess to other metal sulfides. Further, Fe and Mn are rapidly oxidized in well-oxygenated waters, whereas oxidation of Cd, Cu, Pb and Zn is, comparatively, a slower process (Zwolsman 1994; Simpson et al. 1998). However, there is no clear evidence of diagenetic mobilization of Mn or Fe. The distributions of trace metals suggest that either no substantial release of these elements from sediment occurred during resuspension (i.e. the anoxic bed sediment was not eroded), or high concentrations of particulate metals buffer the effects of pore water outflow as a source. The scarcity of information on pore water and dissolved metal data in the study area, however, precludes an assessment of their role. Constancy in particulate trace metal concentrations, nevertheless, indicates that the effects of resuspension of anoxic bed sediments that lie beneath the surficial hydrous layer can possibly be dismissed. Current velocities and possibly shear stress are generally low, and are unlikely to resuspend compacted sediments. Episodic high-flow events, however, where waves and currents can interact and increase the bottom shear stress, could possibly promote sporadic resuspension and redistribution of more consolidated sediments.

Although the acetic acid leach used here is not entirely specific to Fe and Mn (hydr) oxide phases, and metals in each oxide phase cannot be discriminated by a single digest, correlations can be used to empirically assess the role of Fe and Mn in regulating trace metal concentrations. For the five trace metals studied, only Pb presented a significant relationship ($r=0.87$; $P \leq 0.05$) with Mn, suggesting that Mn oxides are an important host phase for Pb. Iron, however, was significantly correlated ($r=0.67$; $P \leq 0.05$) with Cr. For the other elements, no significant correlation was observed with Fe or Mn individually, or when the sum of Fe and Mn was considered. Either the mass of Fe and Mn does not directly control the concentrations of Ni, Cu and Zn, or an undetermined phase (i.e. carbonates, organic matter) is present and also acts as an important sorbent phase.

The two-component (permanent and temporary SPM) particle-mixing model (Morris et al. 1987) used to describe SPM and associated trace metal variations during resuspension processes (Turner et al. 1994; Millward et al. 1998; Williams and Millward 1998) does not apply to the observations of this study. The nonconformity of the results to the particle-mixing model is due to the closeness in the composition of the temporarily resuspended bottom sediments and permanently suspended sediments.

Conclusion

Tidal cycle experiments in the turbidity maximum zone of Port Jackson estuary have shown that concentrations of trace metals and SPM were similar to previous observations (Coutts-Smith 1998; Hatje et al. 2001a). Effects of tidal cycles on the distribution of particulate trace metals and SPM concentrations are relatively minor compared with meso- and macro-tidal estuaries, and are mainly limited to bottom water. However, the estuary is by no means inactive in terms of sedimentary processes. Although sediment exchange between the bottom and the water column do not appear to be significant in controlling trace metal distributions during the tidal cycle, they may be important on smaller spatial scales and/or in the long term.

It is suggested that tidal cycles promote resuspension of a thin hydrous layer of surficial sediments in regular tidal intervals. This surficial hydrous layer had consolidation times of only several hours between resuspension episodes and appears to be easily eroded. As a result of the recycling of this layer, no significant variation was observed in trace metal distributions over a tidal cycle. There is no clear evidence for mobilization of the more consolidated anoxic sediments that lie beneath the surficial hydrous layer.

Under low-flow conditions, current velocities do not seem to exceed the critical shear stress to erode consolidated bed sediments.

In surface water, concentrations of trace metals and SPM did not present significant variability; hence, sample collection for monitoring purposes can possibly be randomly performed within a tidal cycle without significant variation of results. Due to the seaward increase of water depth of the estuary, this conclusion is likely to be applicable to surface waters of the entire main channel of the estuary.

It is recommended, however, that experimental studies compare the influence of river discharges and seasons on the distributions of trace metals. It has been previously observed that concentrations of SPM during winter are significantly lower than in summer (Hatje et al. 2001a). Taylor (2000) has suggested that the presence of algal mats formed in winter months reduce the resuspension of sediments. Biostabilization of sediments, defined as the process whereby microbial growth and the production of extracellular polymeric substances, in conjunction with sediment colonization by algae, result in the increased stabilization of a bed sediment due to the cohesive nature of individual particles and flocs (Tolhurst et al. 1999; Droppo et al. 2001). Hence, the effects of tidal cycle on resuspension processes are anticipated to be even smaller in winter than observed during this study.

References

Allen GP, Salomon JC, Bassoullet P, Du Penhoat Y, De Grandpre C (1980) Effects of tides on mixing and suspended sediment transport in macrotidal estuaries. Sediment Geol 26:69–90

APHA (1995) Standard methods for the examination of water and wastewater, 19th edn. Franson MAH (ed). APHA, Washington, DC

Austen I, Andersen TJ, Edelvang K (1999) The influence of benthic diatoms and invertebrates on the erodibility of an intertidal mudflat, the Danish Wadden Sea. Estuarine Coastal Shelf Sci 49:99–111

Bale AJ, Morris AW, Howland RJM (1985) Seasonal sediment movement in the Tamar estuary. Oceanol Acta 8:1–6

Birch GF (1996) Sediment-bound metallic contaminants in Sydney's estuaries and adjacent offshore, Australia. Estuarine Coastal Shelf Sci 42:31–44

Birch GF, Taylor S (1999) Source of heavy metals in sediment of the Port Jackson estuary, Australia. Sci Total Environ 227:123–138

Calmano W, Forstner U, Hong J (1994) Mobilisation and scavenging of heavy metals following resuspension of anoxic sediments from the Elbe River. In: Alpers CN, Blowes DW (eds) Environmental geochemistry of sulphide oxidation. American Chemical Society, Washington, DC, pp 298–321

Castaing P, Allen GP (1981) Mechanisms controlling seaward escape of suspended sediment from the Gironde: a macrotidal estuary in France. Mar Geol 40:101–118

Chester R, Hugues MJ (1967) A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace metals from pelagic sediments. Chem Geol 2:249–262

Coutts-Smith AJ (1998) Tidal re-suspension of cohesive sediments in the Parramatta River estuary: implications for contaminant dispersal. BSc Hons Thesis, University of Sydney

Das P, Marchesiello P, Middleton JH (2000) Numerical modelling of tide-induced residual circulation in Sydney Harbour. Mar Freshwater Res 51:97–112

Droppo IG, Lau YL, Mitchell C (2001) The effect of depositional history on contaminated bed sediment stability. Sci Total Environ 266:7–13

Duursma EK (1995) Are tropical estuaries environmental sinks or sources? CETEM/CNPq, Serie Technologia Ambiental, 6, Rio de Janeiro

Gelfenbaum G (1983) Suspended-sediment response to semi-diurnal and fortnightly tidal variations in a mesotidal estuary: Columbia River, USA. Mar Geol 52:39–57

Harbison P (1986) Diurnal variations in the chemical environment of a shallow tidal inlet, Gulf St Vincent, South Australia: implications for water quality and trace metal migration. Mar Environ Res 20:161–195

Harris PT, Baker EK, Cole AR (1991) Physical sedimentology of the Australian Continental Shelf, Sydney. Ocean Science Institute, Report 51, Sydney

Hatje V, Birch GF, Hill DM (2001a) Spatial and temporal variability of particulate trace metals in Port Jackson estuary, Australia. Estuarine Coastal Shelf Sci 53:63–77

Hatje V, Rae K, Birch GF (2001b) Trace metal and total suspended solids concentrations in freshwater: the importance of small-scale temporal variation. J Environ Monitor 3:251–256

Heruk B, Kress N (1997) Particulate metals contamination in the Kishon River Estuary, Israel. Mar Pollut Bull 34:706–711

Irvine I, Birch GF (1998) Distribution of heavy metals in surficial sediments of Port Jackson, Sydney, New South Wales. Aust J Earth Sci 45:297–304

Jago CF, Bale AJ, Green MO, Howard MJ, Jones SE, McCave IN, Millward GE, Morris AW, Rowden AA, Williamn JJ (1994) Resuspension processes and seston dynamics, southern North Sea. In: Charnock H, Dyer KR, Huthnance JM, Liss PS, Simpson JH, Tett PB (eds) Understanding the North Sea system. Chapman and Hall, London, pp 97–113

Lindsay P, Balls PW, West JR (1996) Influence of tidal range and river discharge on suspended particulate matter fluxes in the Forth Estuary (Scotland). Estuarine Coastal Shelf Sci 42:63–82

Millward GE, Morris AW, Tappin AD (1998) Trace metals at two sites in the southern North Sea from a sediment resuspension study. Continental Shelf Res 18:1381–1400

Montani S, Magni P, Shimamoto M, Abe N, Okutani K (1998) The effect of a tidal cycle on the dynamics of nutrients in a tidal estuary in the Seto Inland Sea, Japan. J Oceanogr 54:65–76

Morris AW, Bale AJ, Howland RJM, Loring DH, Rantala TT (1987) Controls of the chemical composition of particles populations in a macrotidal estuary (Tamar Estuary, UK). Continental Shelf Res 7:1351–1355

Mulholland PJ, Olsen CR (1992) Marine origin of Savannah River estuary sediments: evidence from radioactive and stable isotope tracers. Estuarine Coastal Shelf Sci 34:95–107

Nichols MM (1993) Response of coastal plain estuaries to episodic events in the Chesapeake Bay region. In: Mehta AJ (ed) Nearshore and estuarine cohesive sediment transport, coastal and estuarine studies 42. American Geophysical Union, Washington, DC, pp 1–20

Niencheski LF, Windom HL, Smith R (1994) Distribution of particulate trace metals in Patos Lagoon Estuary (Brazil). Mar Pollut Bull 28:96–102

Postma H (1967) Sediment transport and sedimentation in the estuarine environment. estuaries. In: Lauff GH (ed) Estuaries. American Association for the Advancement of Science, Washington, DC, pp 158–179

Sanford L, Panageotou W, Halka JP (1991) Tidal resuspension of sediments in northern Chesapeake Bay. Mar Geol 97:87–103

Schoellhamer DH (1996) Anthropogenic sediment resuspension mechanisms in a shallow microtidal estuary. Estuarine Coastal Shelf Sci 43:533–548

Schropp SJ, Lewis FG, Windom HL, Ryan JD, Calder FD, Burney LC (1990) Interpretation of metal concentrations in estuarine sediments of Florida using Al as a reference element. Estuaries 13:227–235

Simpson SL, Apte SC, Batley GE (1998) Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediments. Environ Sci Technol 32:620–625

Taylor SE (2000) The source and remobilization of contaminated sediments in Port Jackson, Australia. PhD Thesis, University of Sydney

Tessier A, Campbell PGC, Bisson M (1979) Sequential procedure for the speciation of particulate trace metals. Analyt Chem 51:844–851

Tolhurst TJ, Black KS, Shayler SA, Mather S, Black I, Baker K, Paterson DM (1999) Measuring the in situ erosion shear stress of intertidal sediments with cohesive strength meter (CSM). Estuarine, Coastal Shelf Sci 49:281–294

Turner A, Millward GE, Tyler AO (1994) The distribution and chemical composition of particles in a macrotidal estuary. Estuarine Coastal Shelf Sci 38:1–17

Uncles RJ, Stephens JA (1996) Salt intrusion in the Tweed Estuary. Estuarine Coastal Shelf Sci 43:271–293

Underwood AJ (1997) Experiments in ecology. Their logical design and interpretation using analysis of variance. Cambridge University Press, Cambridge

Vale C, Sundby B (1987) Suspended sediment fluctuations in the Tagus Estuary on semi-diurnal and fortnightly time scales. Estuarine Coastal Shelf Sci 25:495–508

Vale C, Cortesao C, Castro O, Ferreira AM (1993) Suspended-sediment response to pulses in river flow and semidiurnal and fortnightly tidal variations in a mesotidal estuary. Mar Chem 43:21–31

Williams MR, Millward GE (1998) Dynamics of particulate trace metals in the tidal reaches of the Ouse and Trent, UK. Estuarine Coastal Shelf Sci 37:306–315

Zwolsman JJG (1994) North Sea estuaries as filters for contaminants. Delft hydraulics, report no T1233, The Netherlands