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Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia

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Abstract

Concentrations of dissolved metals (Cd, Cu, Ni, Mn and Zn) were determined for summer and winter, under low-flow conditions in Port Jackson, a microtidal, well-mixed estuary in south-east Australia. Mean concentrations of Cd ($0.04 \pm 0.02 \mu\text{g/l}$), Ni ($0.86 \pm 0.40 \mu\text{g/l}$), Mn ($20.0 \pm 25 \mu\text{g/l}$) and Zn ($6.47 \pm 2.0 \mu\text{g/l}$) were below water quality guidelines. Concentrations of Cu ($1.68 \pm 0.37 \mu\text{g/l}$), however, slightly exceeded recommended values. Dissolved Ni and Mn behaved mostly conservatively, whereas Cd, Cu and Zn showed mid-estuarine maxima. Peaks in Cd, Cu and Zn concentrations were located in the upper estuary, independent of the salinity and suspended particulate matter loading, and were consistent with anthropogenic inputs of metals in the estuary. Concentrations of dissolved Cu were highest in summer, whereas concentrations of Cd, Ni and Mn were significantly lower in summer than winter ($P \leq 0.05$). The increase in temperature and biological activity during summer explained the seasonal variation. The sequence of $\log K_d$ values (20–30 salinity) was $\text{Mn} > \text{Zn} > \text{Cu} > \text{Ni}$. These results give unique information concerning the contemporaneous distribution of dissolved trace metals in the Port Jackson estuary and they provide a data set against which the long-term contamination may be assessed.

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1. Introduction

Although chemical and biological processes are common to all estuaries, the distributions of trace metals and their rates of reactivity vary greatly between estuaries, depending on environmental factors such as hydrodynamic residence times, mixing patterns and transport processes. Hence, there is no universal pattern of trace metal behaviour in estuaries (van der Berg, 1993; Camusso et al., 1997). The same dissolved species, for example Zn, may behave conservatively (Danielsson et al., 1983; Shiller and Boyle, 1991), have mid-salinity maximum (Ackroyd et al., 1986; Laslett and Balls, 1995), or exhibit removal from solution (Windom et al., 1991; Balls et al., 1994). Because of this variety in be-

haviour, it is important to investigate the full range of estuary types, across the entire spectrum of climates, flow regimes, geological terrains and biological communities, to better assess natural variability and to provide a basis for differentiating natural from anthropogenic loads. Moreover, many of the older studies on dissolved trace metals are regarded as unreliable, due to the recent major improvements in field and analytical techniques (Quevauviller, 1997). The awareness of possible analytical problems in “old” studies has led to a renewed interest in dissolved metal distributions in estuaries and their controlling mechanisms.

Many studies have shown that trace metal partitioning between dissolved and particulate phases depends on a number of factors including pH, salinity, temperature, redox-conditions, dissolved organic carbon, and composition of the suspended particulate matter (SPM). The distribution coefficient (K_d) is the most commonly employed means of describing the solid-solution partitioning in aquatic systems, and it is defined as the ratio of particulate concentration (w/w) to

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dissolved concentration (w/v). Strictly, the K_d concept implies true equilibrium and reversibility for the solid-solution reaction. These criteria, however, are frequently either not fulfilled or at least not demonstrated, and consequently, the concept has been widely criticised (e.g. McKinley and Alexander, 1992). As in many cases (e.g. Comber et al., 1995), however, K_d is used in this study descriptively, and does not have implications regarding the state of a reaction.

A considerable amount of research has been conducted to determine the impact of historical and contemporary anthropogenic discharges on trace metal concentrations in the Port Jackson estuary, also known as Sydney Harbour (Irvine and Birch, 1998; Birch and Taylor, 1999; Hatje et al., 2001a). These studies indicated that the elements of greatest concern are Cu, Pb and Zn, due to their elevated concentrations, and potential toxicity to estuarine biota. Hatje et al. (2001b) showed the significance of seasonal and spatial variation of particulate trace metal distributions. It was proposed that significant seasonal variability in particulate concentrations could be explained in terms of change in SPM composition due to biological processes during summer months (Hatje et al., 2001b). There has been, however, surprisingly little work on the concentrations of dissolved metals in Australian waters (Batley, 1996; Apte et al., 1998; Apte and Day, 1998; Munksgaard and Parry, 2001), and so far, no data on dissolved metal concentrations have been published for the Port Jackson estuary.

The aims of this study were, therefore, to investigate the spatial and temporal distributions of dissolved trace metals, as well as the partitioning between dissolved and particulate phases under summer and winter conditions

in Port Jackson, a microtidal, sub-temperate, almost entirely saline estuary.

2. Methods

2.1. Study area

The Port Jackson estuary is a drowned river valley on the south-eastern coastal plain of New South Wales, Australia (Fig. 1). The estuary is about 30 km long and drains an area of approximately 500 km². The catchment, mainly composed of Hawkesbury sandstone and Ashfield shale, is located in the Sydney metropolitan area, and supports the highest population in Australia. Approximately 90% of the catchment is urbanised and/or industrialised, and developments include marinas, refineries, breweries, paint industries, commercial and naval shipping facilities. 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 waters. 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 (Hatje et al., 2001b), as a result of low freshwater discharge and tidal turbulence (Revelante and Gilmarin, 1978). Tides are mixed semi-diurnal with a maximum tidal range of 2.1 m and current velocities range between 0.2 and 0.4 m s⁻¹ (Harris et al., 1991). The bottom sediment in the upper estuary and off-channel embayments consists of muds (>95% mud) and a sandy

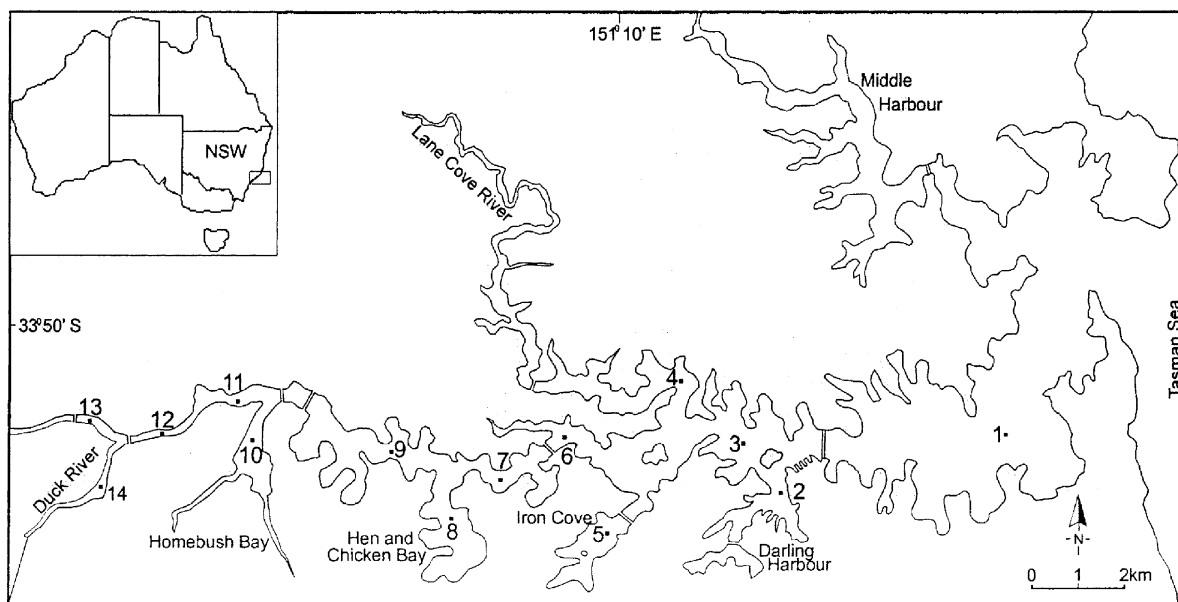


Fig. 1. The Port Jackson estuary, Australia, showing sampling stations.

delta (<1% mud) occupies the estuary mouth (Birch and Taylor, 1999).

2.2. Sample collection and pre-treatment

Samples were collected in February and March 1999 (late summer), July to September 1999 (late winter) and January 2001 (summer) at low slack water, during dry, low-flow conditions. Sampling was undertaken only at low-flow conditions, which represent the typical state of the estuary (i.e. estuary almost entirely saline). Since the water column in the Port Jackson estuary is generally well mixed, only surface samples were collected. Eight stations were selected in the main channel of the Port Jackson estuary (Fig. 1). In each station, water samples were collected in pre-cleaned polyethylene bottles. Bottles and caps were cleaned by soaking for 24 h in a detergent solution (Pyroneg) in a covered tank. They were then rinsed with deionised water (DI; 18 M Ω 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. 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 using acid cleaned, and DI water rinsed 0.45 μ m Millipore (cellulose) filters under clean-room conditions. Filtered water samples were stored in acid cleaned polyethylene bottles and acidified with concentrated nitric acid (1–2 ml⁻¹ Merck Suprapur). A second aliquot of sample, for SPM determinations, was filtered through pre-weighed, acid washed 0.45 μ m Millipore (cellulose) filters. The filters with SPM were rinsed with 20 ml of DI water to remove

salt, dried and subsequently reweighed to obtain the mass of SPM. The results for particulate trace metals are presented elsewhere (Hatje et al., 2001b).

2.3. Chemical analysis

Dissolved Cd, Cu, Ni and Zn (i.e. operationally defined as metals which pass through a 0.45 μ m filter) were analysed by a modified dithiocarbamate-complexation/solvent extraction procedure described by Magnusson and Westerlund (1981). The major modifications were the use of a combined sodium bicarbonate buffer/ammonium pyrrolidine dithiocarbamate (APDC) reagent and 1,1,1-trichloroethane as the extraction solvent instead of Freon (Apte and Gunn, 1987). Sample aliquots (200 ml) were buffered to pH 5–6 by addition of the combined reagent and extracted with two 10 ml portions of trichloroethane. The extracts were combined and the metals back-extracted into 1 ml Merck suprapur concentrated nitric acid. The back extracts were diluted to a final volume of 10 ml by addition of 9 ml of deionised water. The method afforded a preconcentration factor of 20. Cadmium was analysed by GFAAS (Perkin Elmer 4100ZL) using Zeeman-effect background correction. Copper, Ni and Zn were analysed by ICP-AES (Spectro Flame-EOP). Chromium was analysed directly, without preconcentration, by GFAAS (Perkin Elmer 4100ZL) using Zeeman-effect background correction and operation conditions recommended by the manufacturer. Sample concentrations of Cr were, however, below the detection limit (0.42 μ g l⁻¹) and are not presented here. Dissolved Mn was analysed directly by ICP-AES (Spectro Flame-EOP) using salinity-matched standards. To check analytical accuracy, aliquots of CASS-4 (National Research Council of Canada) were analysed with each batch of extractions. Results of analyses of reference material, together with detection limits for metal analyses, are presented in Table 1.

2.4. Statistical analysis

A two-factor analysis of variance (ANOVA) was used to test for spatial and seasonal variability of Cu, Cd, Ni

Table 1
Summary of analytical quality control data for dissolved metals

Elements	Detection limit ^a (μ g/l)	CASS-4 certified value (μ g/l)	CASS-4 measured value (μ g/l)	Spike recovery (%)
Cu ($n = 8$)	0.08	0.592 (0.055)	0.640 (0.046)	108 (7.8)
Cd ($n = 7$)	0.003	0.026 (0.003)	0.024 (0.003)	94 (9.8)
Pb	0.26	0.0098 (0.004)	nd	nd
Zn ($n = 7$)	0.02	0.381 (0.057)	0.418 (0.08)	109 (21)
Cr	0.42	0.144 (0.029)	nd	nd
Ni ($n = 7$)	0.06	0.314 (0.03)	0.326 (0.05)	103 (15)
Mn ($n = 4$)	0.0005	2.78 (0.19)	2.99 (0.24)	100 (7.4)

Average concentrations and standard deviation in brackets; nd = not determined.

^aDetection limit calculated as three times the standard deviation of the procedural blanks ($n = 6$).

and Mn. The number of measurements of Zn was insufficient to test for seasonal and/or spatial trends. Seasonal variability was tested treating the three surveys realized in each season, as independent, replicate measurements. Homogeneity of variances was examined using Cochran's C-test and transformation was not required (Cochran's C-test, $P > 0.05$). Multiple comparisons among the means were performed using Student-Newman-Keuls (SNK) test.

3. Results

3.1. Salinity and SPM concentrations

Mean values for salinity and SPM concentrations are reported in Table 2. Distributions of physico-chemical master variables, detailing temporal and seasonal variability, have been described previously by Hatje et al. (2001b).

Salinity varied over a relatively narrow range during summer and winter. Although a seaward increase was observed in salinity, the estuary was entirely saline under low-flow conditions, i.e. the low salinity zone (salinity 0–5) was absent in the main channel of the estuary. Variations in salinity between seasons were small, and differences were not significant ($P > 0.05$).

Suspended particulate matter concentrations were low (0.5–40 mg/l) at all sampling times. Moreover,

during winter, SPM concentrations were significantly lower ($P \leq 0.05$) than in summer.

3.2. Dissolved trace metals

The spatial distributions of trace metal concentrations are presented in Fig. 2 and the results are included in Table 2. All of the studied metals presented a significant spatial variability ($P \leq 0.05$; Table 3), and basic features of trace metal profiles can be summarised as follows. The Ni and Mn profiles were quite different from those of Cd, Cu and Zn. The latter ones showed a concentration maximum in the mid-estuary. Cadmium showed a gradual increase with increasing salinity, leading to a well-defined peak at relatively high salinity (28–33). The dissolved Cd peak was located around the zone of maximum turbidity. A Cd mid-estuary maximum has also been observed in other estuaries (Elbaz-Poulichet et al., 1987; Kraepiel et al., 1997). Dissolved Cu and Zn profiles also presented a maximum at relatively high salinity, and decreased seawards, following the same behaviour observed for Cd. Maxima in dissolved Cu and Zn profiles have also been observed in Tay estuary (Owens and Balls, 1997) and Scheldt estuary (Monteny et al., 1993; Zwolsman et al., 1997) among other estuaries.

In general, maximum concentrations of Ni and Mn were found in the upper estuary and in the incoming

Table 2
Salinity, SPM and dissolved trace metal concentrations in the Port Jackson estuary

Survey		Salinity	SPM (mg/l)	Ni ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Zn ($\mu\text{g/l}$)	Cd ($\mu\text{g/l}$)	Mn ($\mu\text{g/l}$)
February 1999 $n = 8$	Average	28.5	11.2	0.85	1.97	nd	0.03	14.5
	Std	4.5	8.4	0.41	0.17		0.01	16.9
	Min	20.6	2.3	0.39	1.67		0.01	1.51
	Max	33.5	22.0	1.46	2.23		0.05	52.2
March 1999 $n = 8$	Average	29.2	14.5	0.80	1.63	nd	0.02	19.9
	Std	3.6	12.4	0.38	0.25		0.01	23.7
	Min	23.3	2.1	0.18	1.24		0.01	1.35
	Max	33.3	39.0	1.23	1.94		0.04	64.6
January 2001 $n = 12$	Average	33.9	7.5	0.80	1.98	6.47	0.04	8.14
	Std	1.2	4.2	0.41	0.48	1.99	0.01	8.57
	Min	31.8	1.3	0.29	1.27	3.27	0.02	0.34
	Max	35.1	13.1	1.41	2.55	9.66	0.06	22.0
July 1999 $n = 8$	Average	28.4	5.9	0.87	1.35	nd	0.03	39.2
	Std	5.2	3.8	0.41	0.28		0.02	41.9
	Min	20.9	0.52	0.35	0.93		0.01	2.02
	Max	34.2	10.7	1.45	1.77		0.05	101
August 1999 $n = 8$	Average	30.8	4.4	0.90	1.45	nd	0.06	22.6
	Std	3.0	2.8	0.47	0.32		0.03	23.1
	Min	26.0	0.72	0.36	1.07		0.03	2.02
	Max	34.4	8.5	1.61	1.85		0.10	58.9
September 1999 $n = 8$	Average	31.7	5.1	0.91	1.73	nd	0.07	15.9
	Std	2.9	3.7	0.41	0.23		0.03	18.0
	Min	27.0	1.3	0.37	1.51		0.02	1.35
	Max	34.9	11.5	1.38	2.07		0.10	48.3

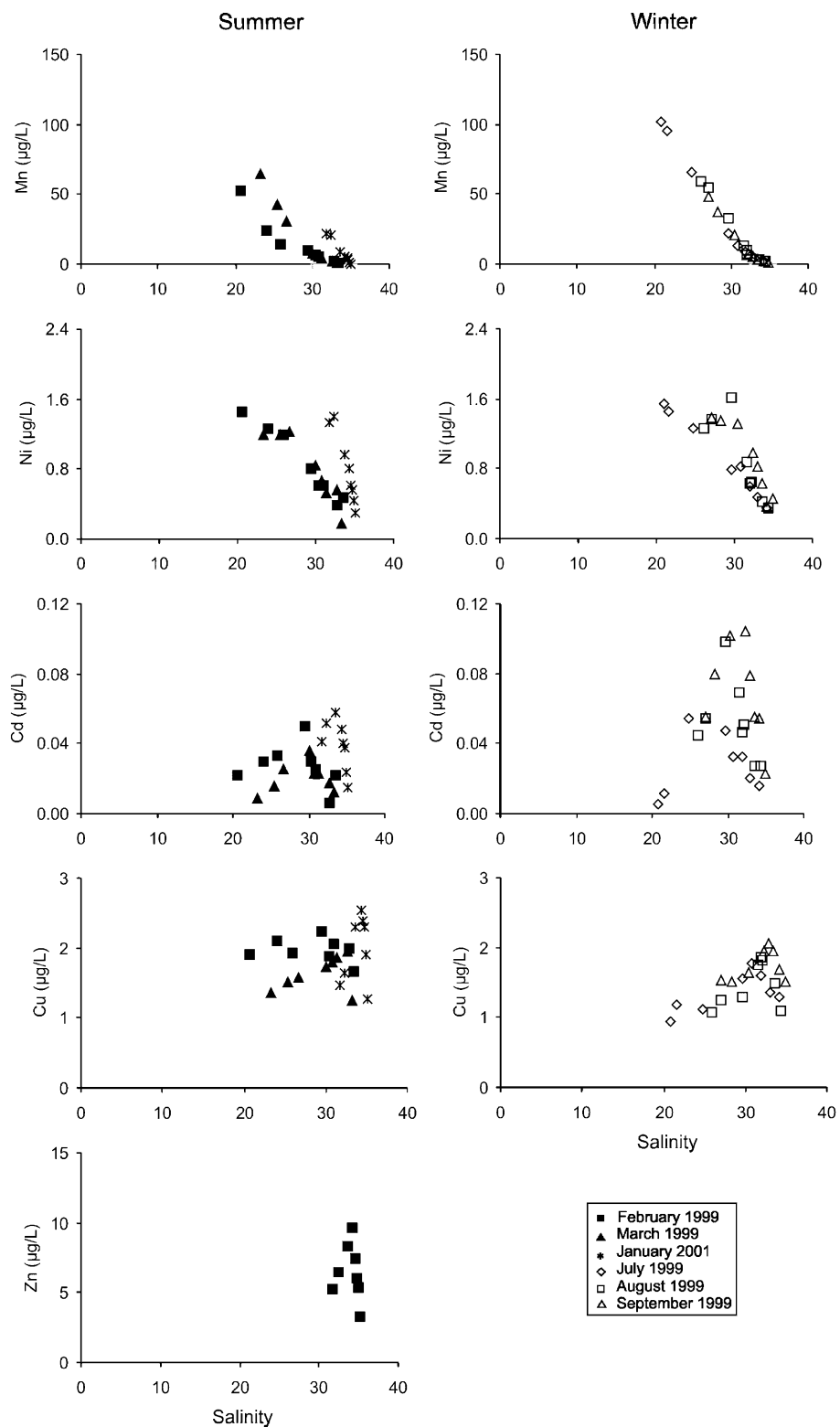


Fig. 2. Distributions of dissolved Mn, Ni, Cd, Cu, and Zn in the Port Jackson estuary.

Parramatta River waters (i.e. Ni; $1.29 \mu\text{g l}^{-1}$ and Mn; $104 \mu\text{g l}^{-1}$ for the January survey). From the upper estuary, the dissolved metal concentrations of Ni and Mn decreased seawards. Although a mid-estuarine maxi-

mum is barely discernible, a positive divergence, in comparison with the theoretical dilution line, within the studied salinity range, i.e. 20–35, was observed for Ni concentrations in the upper estuary.

Table 3

Summary of two-factor analysis of variance of concentrations of dissolved metals in stations and seasons. Each metal was analysed separately

Source of variation	d.f.	Cd			Ni			Cu			Mn		
		MS	F	P	MS	F	P	MS	F	P	MS	F	P
Stations (St)	7	0.0014	3.91	**	1.0068	95.8	***	0.3848	5.82	**	2820	14.7	***
Seasons (Se)	1	0.0051	22.2	**	0.0946	8.15	*	1.4644	34.8	**	1640	6.91	*
St × Se	7	0.0002	0.65	ns	0.0116	1.10	ns	0.0421	0.64	ns	237.5	1.24	ns
Residual	32	0.0004			0.0105			0.0661			191.8		

d.f. = degrees of freedom, MS = mean squares, $F = F$ -ratio test, $n = 3$, ns indicates no significant differences.* indicates significance at $P \leq 0.05$.** indicates significance at $P \leq 0.005$.*** indicates significance at $P \leq 0.001$.

In most cases, metal concentrations were lowest near the estuary mouth. This is to be expected, since Port Jackson acts as a sink for trace metals supplied by rivers and storm water canals that feed the estuary (Taylor, 2000).

The general appearance of summer profiles was repeated during winter, without substantial modifications in metal-salinity plots. Nevertheless, the mean dissolved concentrations of Cd, Cu, Ni, and Mn presented a significant seasonal variability ($P \leq 0.05$; Table 3). Similar to what was observed for particulate trace metals (Hatje et al., 2001b), the variability of dissolved metal concentrations between replicate surveys within each season was smaller than the variability between seasons. Therefore, indicating that small-scale processes were not contributing substantially to the observed temporal patterns. The mean concentrations of Mn, Cd and Ni were significantly lower ($P \leq 0.05$; Table 3) in summer than in winter. Similar seasonal variation of dissolved metals was also observed in Humber estuary (Millward

and Glegg, 1997) and Scheldt estuary (Zwolsman et al., 1997; Bayens et al., 1998). Copper, however, presented the opposite trend, with mean concentrations significantly higher ($P \leq 0.05$; Table 3) in summer than in winter.

4. Discussion

4.1. Significance of dissolved metal concentrations (Cd, Cr, Ni, Mn and Zn)

The results of this study are the first reliable, systematic measurements of dissolved trace metals in the Port Jackson estuary, and some of the first concentrations of dissolved metals reported in any estuary in Australia. Table 4 shows the ranges of dissolved metal concentrations from the present study and also published data for Australian coastal waters and some estuaries elsewhere. As expected, concentrations obtained

Table 4

Dissolved metal concentrations ($\mu\text{g/l}$) in coastal and estuarine surface waters from Australia and estuaries elsewhere

Location	Ni	Cu	Cd	Zn	Mn	Reference
Port Jackson, Australia	0.175–1.61	0.932–2.55	0.006–0.104	3.27–9.66	0.327–101	This study
North Australian coast and estuaries	0.116–0.552	0.151–1.04	0.002–0.034	0.018–0.498	nd	Munksgaard and Parry (2001)
Torres Strait and Gulf of Papua	0.940–4.60	0.036–0.986	<0.001–0.029	nd	nd	Apte and Day (1998)
Open Coastal Pacific Ocean	0.200	0.090	0.010	0.200		Batley (1996)
New South Wales coast, Australia	0.180	0.031	0.002	0.022	nd	Apte et al. (1998)
Port Phillip Bay, Australia	0.540–1.10	0.400–0.630	<0.005–0.070	0.250–1.05		Fabris and Monahan (1995)
Archelos estuary, Greece	2.76	0.31	nd	2.05	5.2	Dassenakis et al. (1997)
Weser estuary, Germany	3.75	2.98	0.16	7.03	7.68	Turner et al. (1992)
Six estuaries, Texas, USA	nd	0.100–3.20	nd	0.300–18.0	nd	Benoit et al. (1994)
Tweed estuary, UK	nd	0.49–4.7	0.007–0.033	0.43–1.90	nd	Laslett (1995)
Humber estuary, UK	nd	0.75–3.6	0.049–0.22	3.6–15	nd	Laslett (1995)
Humber estuary, UK	2.50–12.0	1.80–10.1	0.050–0.450	3.00–20.5	nd	Comber et al. (1995)
Mersey estuary, UK	2.00–10.5	0.80–4.95	0.01–0.11	6.50–28.0	nd	Comber et al. (1995)
Scheldt estuary, Netherlands	nd	0.300–2.22	0.010–0.030	0.600–23.0	nd	Zwolsman et al. (1997)
Tay estuary, Scotland	0.230–0.900	0.450–1.90	0.002–0.120	0.400–8.00	0.001–24.0	Owens and Balls (1997)
Guidelines values ^a	70	1.3	5.5	15	nd	ANZECC/ARMCANZ (2000)

Referenced data are given as average or range data; nd = not determined.

^a Trigger values for marine water with a species protection level of 95%.

in this study were higher than the concentrations of Cu, Cd, Zn and Ni observed for Australian coastal and open waters. Maximum concentrations of trace metals were, in fact, up to 50 times higher than open waters (i.e. for Zn), clearly indicating an anthropogenically derived input of trace metals in the estuarine waters. However, for all metals, the observed concentrations were below the guideline limits for recreational water quality (ANZECC/ARMCANZ, 2000), the main use of the estuarine waters. Compared with the dissolved metal concentrations guideline for the protection of biological species at a level of 95% (ANZECC/ARMCANZ, 2000; Table 4), however, Cu slightly exceeded the recommended values. It has been recognised that availability of metals, and especially of Cu, is of more importance than its total concentration. Speciation of dissolved Cu in natural waters is dominated by interactions with dissolved organic matter (DOM), and the formation of relatively stable Cu-DOM complexes. These complexes are assumed not to be bioavailable, therefore it is unlikely that Cu poses any ecological risk.

The results obtained in this study were comparable to measurements from other industrialised estuaries (Table 4). The good agreement of replicates, reference material results, and the regular trends observed in the trace metal profiles attest the quality of the data.

The elemental Zn:Cd ratio has been used as an indicator of the anthropogenic input to estuarine and coastal waters (Nolting et al., 1999a; Munksgaard and Parry, 2001). In this study, the Zn:Cd ratio was estimated only for one survey in summer, due to the restricted availability of Zn data. Nevertheless, it is expected that the range, and trend observed for this survey is representative of, at least, the summer situation of the estuary, given that the variability among replicate surveys realised in summer and winter months was not significant ($P > 0.05$; Table 3) for any of the studied elements. The elemental Zn:Cd ratios observed here, ranged from 212 to 382 and averaged 298 ± 68 . These values are between the intervals observed for continental rocks, i.e. 600–900 (Taylor, 1964) and oceanic waters, i.e. 5–10 (Nolting et al., 1999a). Compared to other industrialised estuaries also presenting high concentrations of dissolved Zn and Cd, Port Jackson estuary presented higher Zn:Cd ratios. For instance, the range of Zn:Cd ratios for Gironde estuary is 40–60 (Kraepiel et al., 1997) whereas for Scheldt estuary is 38–308 (Duinker et al., 1982). These findings can be explained in terms of the relative abundance of each element, and clearly indicate the significance of anthropogenic emissions of Zn to the estuary. Moreover, this result is consistent with observations of high concentrations of Zn in SPM (Hatje et al., 2001b) and bottom sediments (Irvine and Birch, 1998; Birch and Taylor, 1999; Taylor, 2000) of Port Jackson estuary. Meanwhile, Cd concentrations observed in SPM were below detection limit

(Hatje, unpublished data), whereas Cd concentrations in bottom sediments of the main channel of the estuary are close to background values (Irvine and Birch, 1998).

The ratio of Zn:Cd for Port Jackson marine end-member was 20 times higher than that observed for New South Wales coastal waters (Apte et al., 1998) and North Australian coastal waters (Munksgaard and Parry, 2001). Unfortunately, there are very few published data on dissolved metal concentrations in the freshwater end-members of the estuary to estimate the ratio of Zn:Cd.

4.2. Estuarine trace metal profiles

The steep gradient in salinity, commonly observed in estuaries, is a major controlling factor for the partitioning of dissolved and particulate trace metals. Moreover, the trace metal distributions usually show a very complex pattern relative to salinity. Of the studied metals, only Mn and Ni varied significantly with salinity in Port Jackson ($P \leq 0.05$; Table 5). The absence of a more general dependence of trace metals and salinity may be explained by the restricted salinity range observed here (≈ 20 –35), and the widespread anthropogenic sources of metals to the estuary (Hatje et al., 2001b). Conversely to most estuaries, where Mn shows a non-conservative behaviour, with positive deviations from the theoretical mixing curve at low salinities, and removal at high salinities (Laslett and Balls, 1995; Owens et al., 1997), Mn presented a mostly conservative behaviour (Fig. 2). Nevertheless, this was also observed in Beaulieu estuary (Holliday and Liss, 1976) and Clyde estuary (Muller et al., 1994). During winter, Mn presented a strong inverse correlation with salinity (Table 5) and there was little evidence for removal of dissolved Mn from solution, a situation that can be attributed to the low concentration of suspended solids and low water temperature (Morris et al., 1982). Correlation between salinity and Mn during summer was still high, however, a small negative deviation of the theoretical dilution curve could be observed. The small removal observed in the distributions of dissolved Mn can be interpreted in terms of the fluvial, and possibly, the benthic inputs of Mn (II), being removed from solution by oxidative precipitation of Mn (IV). This process is possibly intensified during summer, as will be discussed below. The behaviour of Ni appears to be linked to that of Mn in marine environments (Laslett and Balls, 1995; Sanudo-Wilhelmy and Gill, 1999). In general, Ni distributions appear to be mostly conservative, and similar to that of Mn (Fig. 2). This similarity in behaviour was attributed to the significant correlation between them (Table 5), suggesting that similar processes influenced both elements. Strong positive correlations were also observed between SPM and dissolved Mn and Ni concentrations during summer and winter

Table 5
Correlation matrix (Pearson-product correlation) for salinity, pH, SPM, and dissolved metal concentrations ($n = 24$)

Variable	Salinity	Temp	pH	SPM	Ni	Mn	Cd	Cu
<i>Panel a: summer</i>								
Temp	-0.85							
pH	-0.38	0.48						
SPM	-0.84	0.86	0.25					
Ni	-0.72	0.69	-0.12	0.78				
Mn	-0.84	0.82	0.22	0.90	0.77			
Cd	0.24	0.95	-0.67	-0.10	0.34	-0.18		
Cu	0.20	-0.20	-0.48	-0.24	-0.04	-0.33	0.57	
Zn ^a	0.08	0.67	-0.48	0.21	0.29	0.05	0.79	0.86
<i>Panel b: winter</i>								
Temp	0.25							
pH	0.80	0.68						
SPM	-0.90	0.04	-0.59					
Ni	-0.80	0.15	-0.45	0.88				
Mn	-0.99	-0.23	-0.78	0.85	0.77			
Cd	0.06	0.55	0.39	0.21	0.46	-0.12		
Cu	0.58	0.32	0.68	-0.38	-0.32	-0.66	0.38	

Bold-type values are significant ($P \leq 0.05$).

^a January survey ($n = 8$).

(Table 5). These correlations reflect the role of physical processes, such as water mixing and bottom sediment resuspension, in the cycling of these metals in the waters. In a resuspension experiment in the turbidity maximum zone of the Port Jackson estuary, Ni was the only element that presented a significant variation over a tidal cycle, following the same behaviour presented by SPM (Hatje, in press). This result attests the importance of physical processes in the distribution of this element. Conservative behaviour of Ni has previously been observed by Shiller and Boyle (1991) and Dai et al. (1995). In a few surveys, both in summer and winter, dissolved Ni distributions vs. salinity show a small addition phenomenon in the upper estuary, in the turbidity maximum zone, and simple dilution thereafter.

A large mid-salinity maximum in dissolved Cd concentrations is a typical feature of many estuaries (Elbaz-Poulichet et al., 1996; Kraepiel et al., 1997; Zwolsman et al., 1997). It has been usually explained in terms of the release of Cd from the particulate phase, because of increasing complexation by chloride at higher salinities (Comans and Van Dijk, 1988). The stability and the solubility of the chlorocomplexes formed enhance the mobilisation of Cd in estuaries and usually prevent the competing readsorption processes from occurring (Elbaz-Poulichet et al., 1987). The maximum in dissolved Cd concentration was a consistent feature through all surveys, and was localised downstream from Homebush Bay (Fig. 1). The permanent occurrence of Cd maxima in the same location, independent of the salinity or SPM concentrations, appears to be dominated by point source inputs. Concentrations of Cd in bottom sediments of Port Jackson estuary are generally low in the main channel of the estuary (Taylor, 2000). As such,

pore water injection, due to resuspension processes, is not expected to be important in the main channel. Moreover, in low turbidity microtidal estuaries, the contribution of resuspended particles to dissolved Cd maxima is expected to be very limited due to the low concentration of these particles in the mixing zone. High concentrations of Cd, however, were observed in fluvial sediments of stormwater canals, steeply decreasing away from sources (Taylor, 2000). Remobilization of Cd from sediments of embayments, especially in Homebush Bay, can possibly account for a major increase in Cd concentrations. However, more data, especially on particles, are needed to provide a better understanding of the respective contribution of suspended and deposited sediments on the distributions of dissolved Cd.

During the January survey, Cd concentrations were positively correlated ($r = 0.78$; $P \leq 0.05$) to phosphate, indicating that Cd maxima could also be associated with phosphate regeneration. Dai and Martin (1995) and Owens and Balls (1997) also observed similar relationships between Cd and phosphate.

Dissolved concentrations of Cd were also significantly correlated ($P \leq 0.05$; Table 5) to those of Zn and Cu, during summer. The mid-estuarine peak in dissolved Zn was as pronounced as Cd. Nevertheless, Cu presented a broader peak. Desorption or dissolution from riverine particles and/or from resuspended sediments has been proposed to be responsible for the addition of dissolved Cu and Zn in other estuarine environments (Elbaz-Poulichet et al., 1987; Bayens et al., 1998). As for Cd, in addition to competitive sorption by seawater cations, dissolved Zn is increasingly complexed by chloride ions as salinity increases. The degree and the nature of the complexation (organic and/or inorganic),

however, cannot yet be assessed, as speciation data for these metals, and concentrations of complexing ligands are unknown. Seawards from the estuarine maxima, concentrations of Zn, and Cu decreased, possibly due to readsorption onto SPM and dilution. For Cu and to a lesser extent Zn, the hypothesis of readsorption by particulate matter is supported by a mirrored increase in particulate metal concentrations (Hatje et al., 2001b), while dissolved metal concentrations decrease in the lower estuary. The behaviour of dissolved and particulate Cu and Zn concentrations, in the lower estuary, is certainly not only related to sorption, but also modified by anthropogenic additional inputs. The high anthropogenic inputs of dissolved Cu and Zn (Barry et al., 2000) and sediment–water exchange processes are probably accountable for the establishment of the mid-estuarine maximum. Nevertheless, a higher resolution spatial sampling design would be necessary to eliminate the uncertainties associated with identifying the sources and processes controlling the behaviour of dissolved metals.

4.3. Seasonality

Understanding the causes of seasonal variability in dissolved trace metal concentrations in estuaries can be complicated by interrelationships among potential controlling factors and anthropogenic inputs. Dissolved trace metal concentrations generally show empirical relationships with discharge (Shiller, 1997). The significant temporal variation observed (Table 3, Fig. 2) in this study is, however, unlikely to be associated with variations in freshwater discharge, since all surveys were undertaken during low-flow conditions. Upper Paramatta River discharges at all sampling times varied in the narrow range of $0.1\text{--}1.7\text{ m}^3\text{ s}^{-1}$. Hence, seasonal variation in trace metal concentrations cannot be simply related to factors such as the river discharge or SPM loads.

Temperature was significantly correlated with Mn and Ni during summer (Table 5), suggesting a temperature-driven effect on these metal distributions. Most likely, the balance between oxidation and reduction rates determines Mn concentrations. Changes in this balance may well affect not just the dissolved concentrations of Mn, but also the concentrations of elements sorbed by oxide surfaces, i.e. Zn, Pb and Ni (e.g. Shiller and Boyle, 1991; Heal, 2001). Concentrations of Mn and Ni were significantly lower ($P \leq 0.05$; Table 3) in summer than in winter. This variation in Mn concentrations possibly reflects the oxidation of Mn (II) to Mn (IV). During winter, Mn showed a preference for the dissolved state, whereas during summer, in average, $60 \pm 13.7\%$ of Mn was in the particulate state. There is ample evidence that the oxidation of Mn is typically bacterially mediated, and that this process is more efficient in warmer temperatures, resulting in lower con-

centrations of dissolved Mn during summer (Sunda and Huntsman, 1987; Cossa et al., 1990; von Langen et al., 1997). Concordant to Mn, the Ni content in the dissolved phase was lowest in the summer period and it is possibly controlled, at least in part, by coprecipitation with Mn.

The low dissolved concentrations of Cd during summer might be explained by a removal process. Since phytoplankton is blooming during this period (i.e. high chlorophyll-*a* concentrations, high saturation in dissolved oxygen, high pH; Hatje et al., 2001b) it is tempting to ascribe the removal of dissolved Cd and, perhaps, Zn to biological uptake. The involvement of trace metals in biological cycles in estuaries is well established (e.g. Shiller and Boyle, 1991; Tappin et al., 1995). Moreover, dissolved Cd and Zn presented a significant relationship with dissolved Si (Cd, $r = 0.98$; Zn, $r = 0.71$; $P \leq 0.05$) for the January survey (i.e. the only survey during which nutrient data was collected). Indirectly, phytoplankton blooms may also affect trace metal concentrations by increasing the pH, which may favour sorption onto suspended matter. The pH in the estuary during summer was up to 1 pH unit higher than the pH observed during the rest of the year (Hatje et al., 2001b). The lack of Cu removal during summer might be related to the strong association between dissolved Cu and dissolved organic Cu-complexing agents, e.g. humic and fulvic substances and organic material excreted by phytoplankton, which can prevent biological uptake (Gerringa et al., 1996). Therefore, temporal variations in dissolved Cu concentrations are possibly associated with the seasonal availability and origin of organic ligands.

4.4. Distribution coefficients (K_d)

The distribution coefficients (Fig. 3) provide empirical information on the combined effect of heterogeneous reactions on the solid-solution distribution of an element. An elevated K_d value indicates affinity of an element to be associated, and transported with the solid phase. Hence, K_d s are of fundamental significance to geochemical modelling and pollution impact assessment (Ng et al., 1996).

As noted by Balls (1989), variations in K_d values in areas of salinity greater than 20 are not influenced to a great extent by differences in physico-chemical parameters (i.e. salinity, pH). This appears to be the case for Cu and Ni, between salinities 20 and 30. Nevertheless, a small increase in K_d values was observed at higher salinities, especially during summer (i.e. high SPM concentrations and biological productivity), suggesting a change in the partitioning of trace metals in the lower estuary. Increased association of trace metals to particles at high salinities favours the retention of Cu, Ni, Zn and Mn in the estuary since net particle transport in the

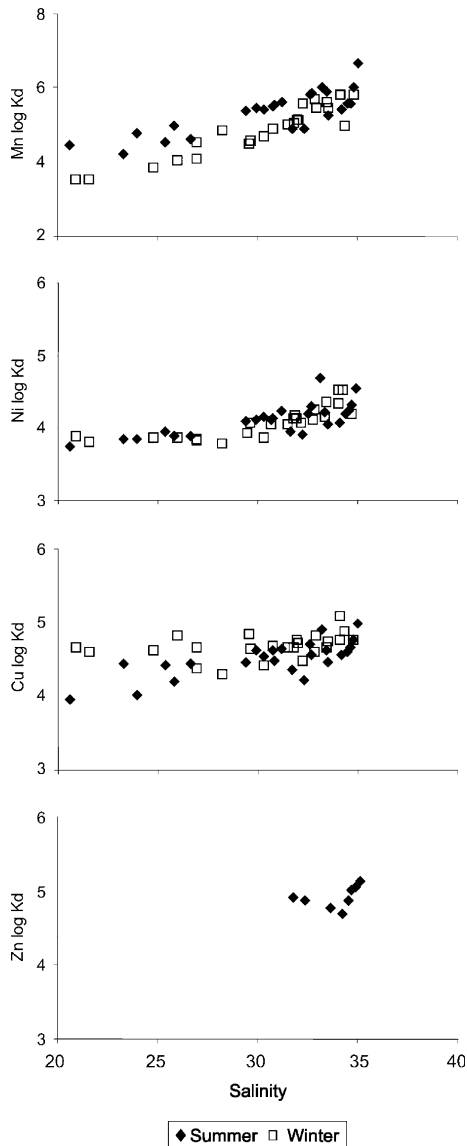


Fig. 3. Partitioning coefficients ($\text{Log } K_d$) of Mn, Ni, Cu and Zn as a function of salinity. Particulate metal concentrations from Hatje et al. (2001b).

coastal zone is generally directed landward. The K_d variations between seasons were not significant for Ni and Cu, suggesting that seasonal factors are of minor importance in the partitioning of these metals.

Values of K_d for Mn increased with salinity, hence with dissolved oxygen, water temperature and pH (Hatje et al., 2001b). The oxidation of dissolved Mn in the water column and formation of solid (hydroxy) oxides is, possibly, the main cause for this change in K_d . The rate of Mn oxidation seems to be controlling its partitioning in the estuary, and it is probably slower in winter than in summer, perhaps due to lower temperatures, lower SPM and reduced bacterial activity (Keeney-Kennicutt and Presley, 1986).

As salinity and SPM concentrations were inversely correlated ($P \leq 0.05$; Table 5), the increase of the parti-

tion coefficients seaward is not only related to the increase in salinity, but also to the decrease in SPM concentrations (Fig. 4). The fact that salinity and SPM concentrations covaried, i.e. are not independent, makes the individual interpretation of the influence of each variable on the K_d distributions confounded. Hence, there is no way to attribute causality to the observed K_d increase seawards. Nevertheless, many studies have described the decline of K_d values with increasing SPM concentrations as the 'Particle Concentration Effect' (O'Connor and Connolly, 1980), without acknowledging this confounding influence.

The range of K_d values observed here are in good agreement with those reported for other estuaries (e.g. Paucot and Wollast, 1997; Nolting et al., 1999b;

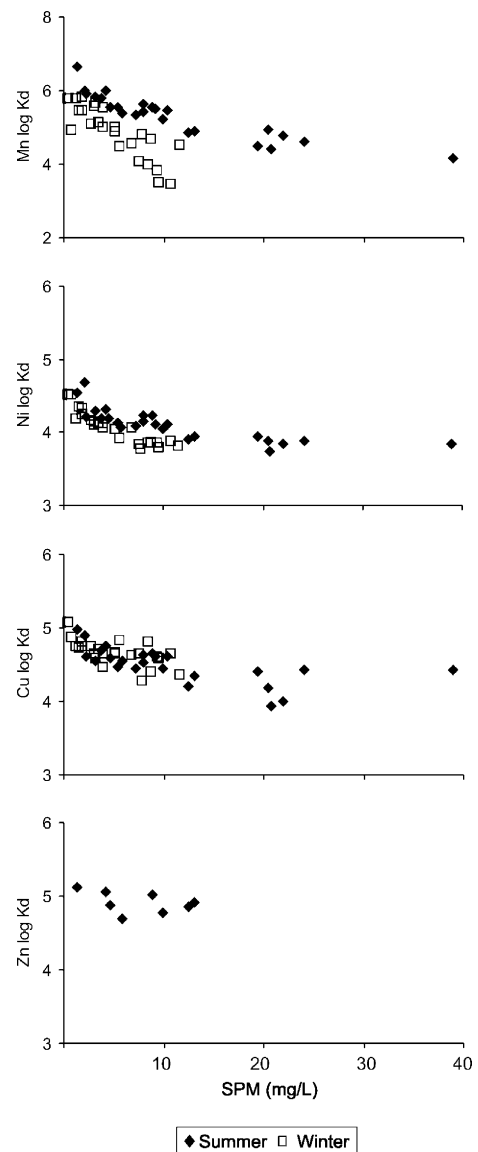


Fig. 4. Partitioning coefficients ($\text{Log } K_d$) of Mn, Ni, Cu and Zn as a function of SPM concentrations. Particulate metal concentrations from Hatje et al. (2001b).

Wen et al., 1999). The sequence of magnitude for K_{ds} from Port Jackson estuary (20–30 salinity) is $Mn > Zn > Cu > Ni$. This sequence is based on average values over the whole estuary.

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