

Contaminant dynamics in offchannel embayments of Port Jackson, New South Wales

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Iron Cove, Hen and Chicken Bay, Homebush Bay, and Rozelle/Blackwattle Bay are offchannel embayments on the southern shoreline of Port Jackson. These shallow (<8 m water depth) embayments are mantled by bioturbated surficial sediments of easily resuspended oxic material (>90% mud), termed the 'hydrous layer'. Sediment in these offchannel embayments is highly enriched in metallic and organic contaminants and each embayment is characterised by a distinct ratio of heavy-metal concentrations. Heavy-metal concentrations and total-organic and sulphur contents of sediments decrease rapidly seaward from stormwater canals and other point sources.

Sediment traps deployed at six locations in Iron Cove, each week for two periods of 16 and 26 weeks, provide time-integrated samples and settling rates of particulate matter from the overlying water column. Settling rates recorded during summer deployments were four times higher than during winter. Comparable

heavy-metal concentrations between settling particulate matter and the ambient hydrous layer at each trap location imply that the majority of the trapped material is derived by resuspension. The relative contribution of the many processes which may resuspend surficial estuarine sediment, e.g. physical (wind-generated waves, tidal action, stormwater runoff), biogeochemical (bioturbation, flocculation and dispersion), and anthropogenic (trawling, boating, engineering construction) are discussed.

The implications of these findings are that toxicants bound in sulphidic sediments are continuously remobilised into the water column. Resuspension and secondary sourcing of highly contaminated sediments probably occurs in many of the extensive shallow water environments of Port Jackson and other affected estuarine systems, thereby providing a pathway for contaminants to enter the foodchain.

Introduction

Sediment resuspension may be defined as 'reconveying particles which have been deposited on bottom sediments into the overlying water column' (Bloesch 1995). This important process of redistributing particulate material and associated contaminants is being widely studied in Europe and North America, mainly in lacustrine environments (Bloesch & Evans 1982, Rosa 1985, Hilton et al. 1986, Bloesch 1994, Weyhenmeyer et al. 1995). Resuspension occurs wherever bottom shear stress overcomes the cohesion of the sediments and is not restricted to shallow water. Resuspension of sediments may be due to meteorological, hydrological or anthropogenic processes and may be periodic (e.g. tidal cycling) or non-periodic (e.g. ephemeral wind-generated currents). In some lakes, resuspension is the dominant process (approximately 85% of gross sediment flux) of transporting bottom sediments into the water column (Evans 1994).

Offchannel embayments of the southern shoreline in Port Jackson are highly contaminated from a variety of sources and contemporary contamination is occurring through stormwater canals that drain into these receiving waters (Shulkins 1994). Iron Cove, Hen and Chicken Bay, Homebush Bay and Rozelle/

Blackwattle Bay are shallow embayments (generally <8 m water depth) that have been extensively reclaimed (and contained by sea walls) (Fig. 1). Tidal range within the embayments is <2 m and intertidal mud flats are exposed in bay ends. Within embayments, sandy shoreline sediments generally fine to highly bioturbated muds in deeper water. A surficial layer (up to 3 cm thick) of easily resuspended, low-density, oxic sediment, termed the 'hydrous layer', overlies compacted oxic and anoxic sediments in parts of the bays. Hydrous material occurs extensively throughout all Sydney's estuaries (McCleod & Birch 1995, Shotter et al. 1995, Birch et al. 1996) and thus the implications of this research are widespread.

Heavy metals are toxic to many marine species, some of which accumulate heavy metals that may be incorporated into the food chain. The majority of heavy metals in an estuarine system are associated with particulate matter rather than the dissolved phase and, hence, understanding the processes that resuspend settled material is critical to understanding contaminant dispersal. This paper deals with the spatial distribution of contaminants and processes of resuspension in offchannel embayments of Port Jackson.

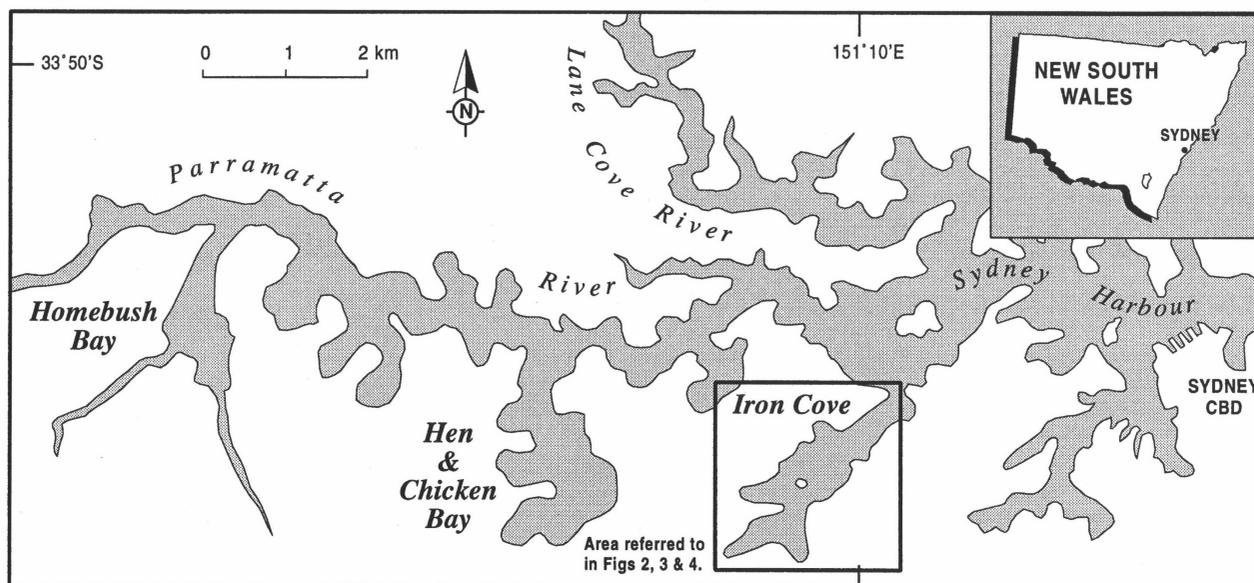


Figure 1. Location map, Port Jackson.

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Methods

Sediment samples from 140 locations in the embayments were collected, using box and push corers (maximum depth 0.3m). Subsamples of the hydrous layer and oxic and anoxic sediments were size normalised by wet sieving with ambient water through 63 μm nylon mesh, digested with a strong acid solution (2:1 concentrated perchloric:nitric) and analysed for eight elements (Cu, Pb, Zn, Ni, Co, Mn, Cd, Fe) by flame atomic absorption spectrometry (FAAS).

Sediment traps were deployed at six locations in Iron Cove each week for 16 weeks from December 1994 to March 1995 and for 26 weeks from July 1995 to January 1996 to collect settling particulate matter (SPM). The sediment traps consist of a polycarbonate tube (600 mm by 79 mm I.D.), sealed at one end with the open end held vertically 0.5 m above the sediment by a concrete block. The height to width ratio of the traps is such that resuspension of SPM out of the traps is unlikely under normal conditions (Bloesch & Burns 1980). At sites 1, 4 and 5, sediment traps were also deployed at heights of 0.25 and 1.5 m above seabed. The short period of deployment (less than 8 days) meant that the traps did not require poisoning to prevent organic matter metabolism of the oxic SPM. The trap locations were determined by water depth and proximity to canal mouths (Fig. 2). Divers also sampled ambient surficial sediment (or hydrous layer) when each sediment trap was collected. The entire SPM and surficial sediment sample was dried, weighed and analysed, as for sediment samples. Internal laboratory standards (ILS), duplicates, standard reference materials (SRM) (e.g. Mag-1) and blanks were run with all digestions. Analytical precision for ILS and duplicates was better than 10% relative standard deviation (RSD) and determinations of SRM were within accepted ranges. Total carbon (TC) and sulphur were determined using a Leco carbon/sulphur analyser. Total organic matter content was estimated by weight loss on ignition (LOI) after heating to 550°C for three hours (precision was 5% RSD). Sediment and SPM samples from Iron Cove were analysed by laser particle sizing and XRD for grain size and clay mineralogy.

Results

The highest mean value for Cu in Port Jackson sediments occurs in Hen and Chicken Bay (Table 1), whereas Iron Cove and Rozelle/Blackwattle Bays have the highest mean Pb concentrations. Homebush Bay has the highest mean Cd concentration. Zn, Cd and Pb concentrations in sediments decrease rapidly seawards from stormwater canals in Iron Cove (Figs 3, 4) and Rozelle/Blackwattle Bays. Similar trends occur in Hen and Chicken Bay, with Cu values decreasing down the bay from relatively high concentrations at the bay end. Heavy metal concentrations in sediments of Homebush Bay are dominated by localised industrial sources on the eastern side of the bay. Total heavy metal concentrations vary only marginally downcore (to a maximum of 0.3 m) across the redox boundaries; however, element speciation is expected to be considerably different in oxic and anoxic sediments.

The present study has focused on sediments and SPM in Iron Cove. Throughout the deeper sections of the embayment, sediments are predominantly muds (>90% <63 μm) and laser particle sizing indicates that the majority of the fine fraction is silt sized (90% >4 μm). XRD analysis of the sediment shows the muds from Iron Cove to be composed almost entirely of quartz and kaolinite. SPM is composed of aggregates, or flocs of finer material and faecal pellets. Total organic matter content for both sediment and SPM, as estimated by LOI, decreases away from stormwater canals from 15 to 12%. No significant differences in total organic matter content or TC results were recorded from SPM samples collected in summer or winter, nor in SPM collected at different heights in the water column. Inorganic carbon content of the sediment is low (disregarding shells) and, hence, the TC of the sediment closely approximates total organic

Table 1. Mean, maximum and minimum (<63 μm) sediment concentrations of Cu, Pb, and Zn in offchannel embayments ($\mu\text{g}\cdot\text{g}^{-1}$).

		Cu	Pb	Zn	Cd
Hen & Chicken Bay n=29	Min.	145	265	580	0.5
	Max.	950	900	1600	3.8
	Mean	345	344	798	0.9
Homebush Bay n=23	Min.	90	220	650	1.5
	Max.	130	400	1000	3.9
	Mean	116	232	783	3.5
Iron Cove n=28	Min.	135	330	650	<0.3
	Max.	290	900	1350	11.4
	Mean	225	520	908	2.5
Rozelle/Blackwattle Bay n=21	Min.	50	65	185	0.3
	Max.	480	2100	2550	6.0
	Mean	210	510	820	1.7

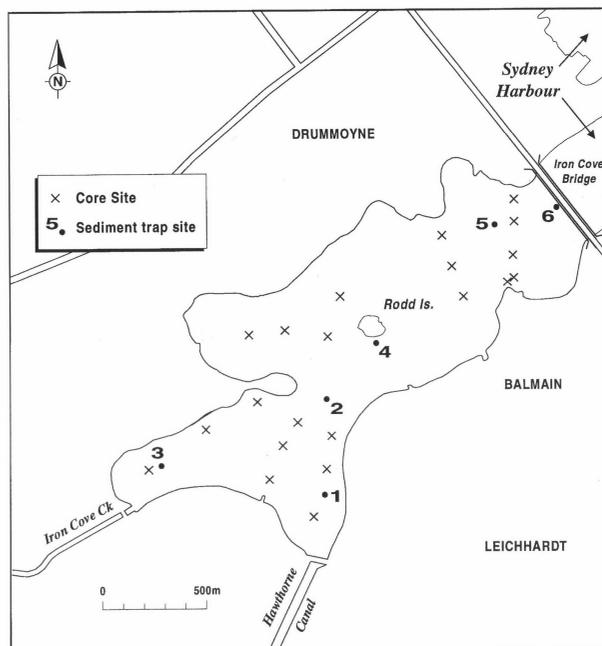


Figure 2. Sediment and sediment trap sampling locations.

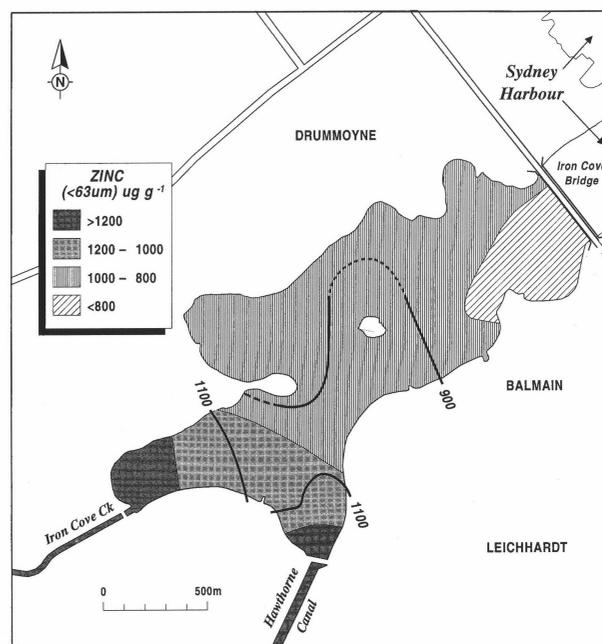


Figure 3. Zn distribution in <63 μm sediment fraction ($\mu\text{g}\cdot\text{g}^{-1}$).

carbon content. TC content of sediments and SPM decreases slightly down the embayment from 6.9 to 3.8% and 5.2 to 3.3% respectively. Similarly, total sulphur content of sediment and SPM also decreases away from stormwater canals from 1.60 to 0.43% and 1.26 to 0.48% respectively. The cation exchange capacity of sediments in Iron Cove is very low (53–87 milli equivalents.kg⁻¹) and increases slightly away from the source of heavy metals (pers. comm. D. McConchie 1996). Binocular microscope examination of the coarse fraction (>63 µm) of the sediment revealed accumulations of hydrocarbons ('tarballs'), which decrease in size and abundance away from the canals. Analysis of the extractant from acetone digestion of these hydrocarbons has shown that heavy metals are associated with the tarballs.

Settling rates, determined by gross flux in sediment traps, varied from 2 to 9 g.m⁻².d⁻¹ in the summer of 1996 (deploy-

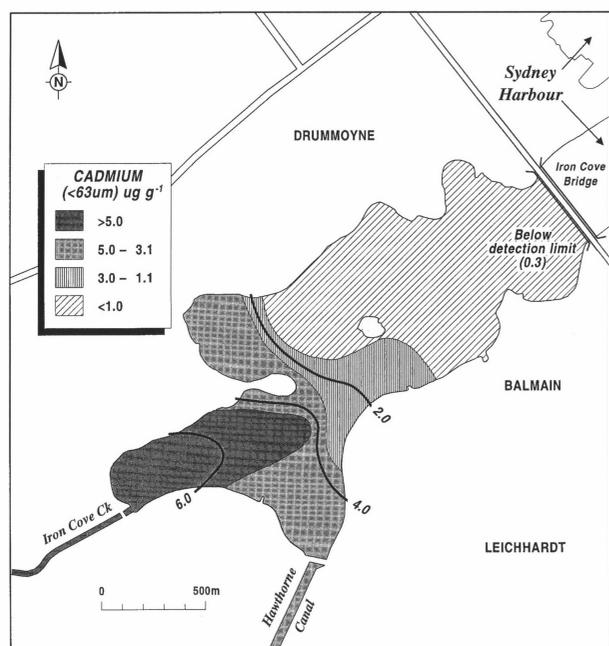


Figure 4. Cd distribution in <63 µm sediment fraction (µg.g⁻¹).

ments 1–14), but were more erratic and often considerably higher in deployments 30–42 (Fig. 5). Winter settling rates were consistently low, averaging approximately 1 g.m⁻².d⁻¹. The weekly trends of settling rates are generally consistent between sites throughout Iron Cove. Traps stacked vertically show the SPM to be distributed throughout the water column, but increasing in settling rate towards the sediment/water interface. Heavy metal concentrations of the SPM are high (e.g. Cu 170–280 mg.g⁻¹, Pb 365–750 µg.g⁻¹, Zn 700–1100 µg.g⁻¹) and decrease seawards, paralleling the concentration trends in the sediments. SPM heavy metal concentrations exhibit low temporal variation under normal meteorological (low flow) conditions. A period of heavy rain in March 1995 produced a thin, buoyant, turbid, freshwater plume that persisted for ten days.

Discussion

Pre-anthropogenic concentrations of heavy metals calculated from analysis of cores (Irvine 1980) provide background values that are used to determine enrichment (Table 2). The four embayments have mean enrichments over 10 times background concentration for Cu, Pb and Zn and maximum enrichment for Cu in Hen and Chicken Bay is 95 times background. Maximum enrichment for Cu, Pb and Zn is almost 30 times background in Iron Cove and approximately 50 times background in Rozelle/Blackwattle Bay.

The distribution of Cu and Pb in surficial sediments of Iron Cove sediments is similar to that of Zn (Fig. 3), with the two

Table 2. Enrichment of Cu, Pb and Zn in embayment sediments over background values.

		Cu	Pb	Zn
Background (µg.g ⁻¹)		10	33	47
Hen & Chicken Bay	Max.	95	27	34
	Mean	35	10	17
Homebush Bay	Max.	13	12	21
	Mean	11	10	17
Iron Cove	Max.	29	27	29
	Mean	23	16	19
Rozelle/Blackwattle Bay	Max	48	63	54
	Mean	21	15	17

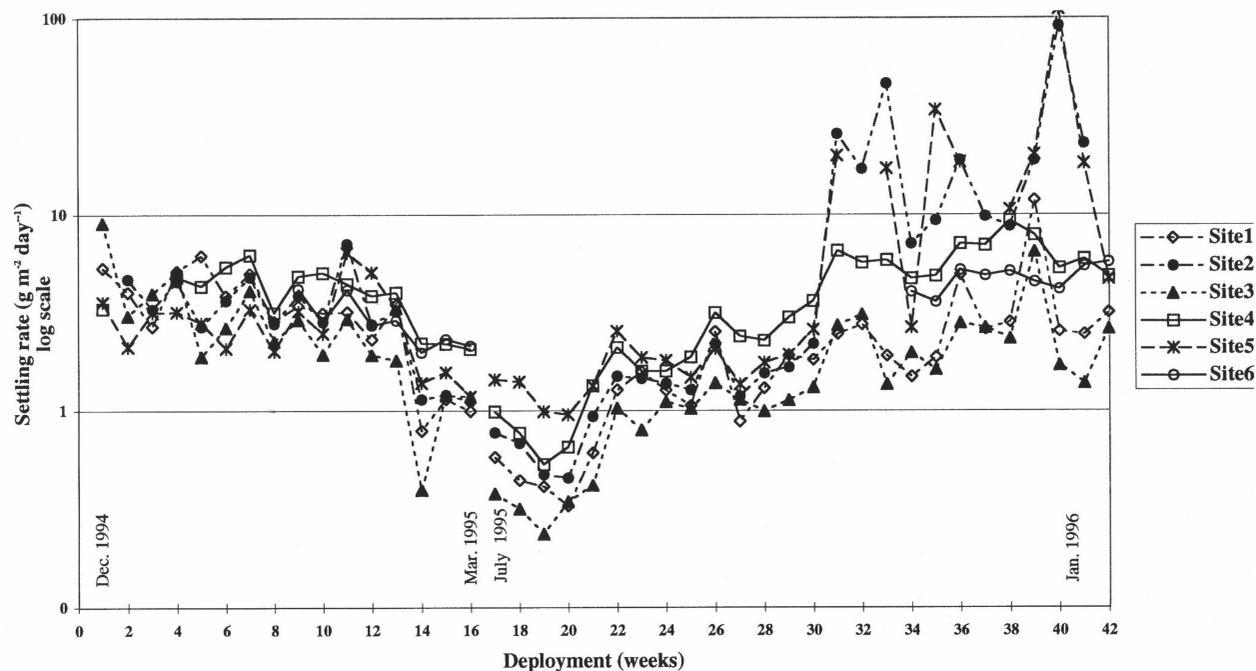


Figure 5. Settling rate determined by sediment traps, Iron Cove.

stormwater canals contributing equally to heavy metal loads, whereas the distribution of Cd is dominated by input from Iron Cove Creek (Fig. 4). Large quantities of contaminated sediments entering Iron Cove and Hen and Chicken Bay via stormwater canals constitute an important contemporary source of toxicants (Shulkins 1994). High levels of heavy metals in soils of the Glebe area (Markus 1993) may indicate that contaminated soils have been an important source of heavy metal contaminants into Rozelle/Blackwattle Bay and Port Jackson generally. Groundwater, particularly leachate from landfill at bay ends, is another potential source of heavy metal contaminants.

Pb, Zn and Cd concentrations in Iron Cove sediments decrease rapidly seaward from stormwater canals, coincident with increasing water depth. Cu, Ni and Co concentration gradients are less pronounced and Mn concentration increases slightly with increasing water depth. Mn concentration does not reflect anthropogenic sources, but rather the redox conditions required for stable deposition. The heavy metal concentrations of the sediment are not spatially related to sediment grain size variation, mineralogical changes or cation exchange capacity. Redox conditions and pH of the sediments (Baker & Harris 1993) also do not vary systematically with distance from source. Heavy metal distribution is probably related to proximity to source, with sediments efficiently binding contaminants in oxic and sulphidic phases. TOC and total sulphur concentrations and, possibly, hydrocarbon accumulations may also be important controls of heavy metal distribution, as these parameters parallel the general trend of heavy metal concentration. Upper reaches of Rozelle/Blackwattle Bay, including Darling Harbour, contain sediments highly enriched in Pb and Zn, but decrease rapidly seaward, possibly due to dredging. Investigation of the influx of contaminant into offchannel embayments is continuing.

Comparing sediment values with toxicant concentrations derived from biological effects-based criteria may assess toxicity of heavy metals in these embayments. The threshold values for initiation of detrimental effects for sensitive biota are; Cu $70 \mu\text{g.g}^{-1}$, Pb $35 \mu\text{g.g}^{-1}$, Zn $120 \mu\text{g.g}^{-1}$, and Cd $5 \mu\text{g.g}^{-1}$. Sediment concentrations of more than Cu $390 \mu\text{g.g}^{-1}$, Pb $110 \mu\text{g.g}^{-1}$, Zn $270 \mu\text{g.g}^{-1}$, and Cd $9 \mu\text{g.g}^{-1}$ are known to frequently or always affect biota (Long & Morgan 1990). Pb and Zn in sediments in Iron Cove, Hen and Chicken Bay, Homebush Bay and Rozelle/Blackwattle Bays are above levels known to be detrimental to biota. Cu values in these embayments are above threshold toxicity levels, whereas Cd in toxic concentration is restricted to the upper reaches of Iron Cove.

Sediment traps collect a sample that represents the particulate material present in the water column at the trap location during the period of deployment. This time-integrated particulate sample originates from influx of allochthonous material (stormwater runoff and direct atmospheric contribution), primary production by the biota in the water column (especially phytoplankton), and resuspension of previously deposited material. To determine the component of allochthonous material in SPM, rainfall recordings were averaged and used to indicate the volume of stormwater runoff entering Iron Cove. While this method does not directly measure the contribution of highly variable stormwater influx to settling rates, only a poor correlation between heavy rainfall and increased settling rate was observed. The contribution of atmospheric particles to the SPM is assumed to be negligible. Biomass input may vary seasonally; however, no significant change was observed in TC or total organic matter content of SPM.

The two processes that transport previously deposited dissolved contaminants back into the overlying water are direct diffusion from the benthic layer and, more importantly, mass transfer (Cheng et al. 1995). As shear stress increases, increased total metal concentrations in the water column are related to particulate material increase and not dissolved phases (Slotton & Reuter 1995). Processes such as tidal or wind-wave-generated water movement and anthropogenic activities can cause an

increase in shear stress and resuspension of sediments in shallow embayments. SPM settling rates over 4 months in summer 1994–5 varied cyclically and in unison with tidal variation. A correlation between settling rate and mean tidal variation implies tidal resuspension is an important process in contaminant dynamics of the embayments. The effect of wind-generated waves in resuspending sediments in shallow water was observed at site 3 during a period of strong northeasterly wind in the first trap deployment (Fig. 5). Wind-wave-generated resuspension is highly variable and dependent on wind velocity, direction, duration and fetch.

Sediment resuspension and a subsequent increase in SPM collected in the centre of the bay (sites 2 and 5) occurred during a two-week period of prawn trawling in Iron Cove (deployments 11 and 12). A substantially greater effect of trawling was observed in deployments 30–42 over the summer months of December–January 1995–6, when rainfall and other conditions were favorable for prawning and settling rates reflect large amounts of sediment being resuspended. Divers observed furrows, up to 8 cm deep in the surficial sediment, which had been created by 'otter boards' used to keep the mouth of prawn nets open and close to the seabed. During the prawning season, from November to April, up to 20 vessels were recorded trawling in Iron Cove. The amount of particulate material resuspended is 10–100 times greater than attributable to natural processes. Trawling and wind-wave-related processes of resuspension were ephemeral or spatially restricted. The cyclical pattern of settling rates observed over the summer of 1994–5 was not apparent over the same period in the following year. This is probably due to very large quantities of SPM from intense prawn trawling overprinting the subtler trend.

A strong spatial correlation of the SPM and surficial hydrous sediment heavy metal concentration indicates that the suspended material is derived directly from the embayment floor. SPM collected at each trap location in Iron Cove was marginally lower in heavy metal concentration than sediments surrounding the trap site (Fig. 6). This divergence of Pb, Zn and Cd concentrations is more apparent at sites in shallower water, implying either dilution by autochthonous organic matter (primary production of biomass) or allochthonous material, or that resuspended material is derived from a source of lower heavy metal concentration (assuming conservative behavior). Cu does not show a similar divergence in concentration, and the gradient is less pronounced. A limited number of sediment and SPM analyses for organochlorine pesticide residues indicate that the SPM is not only a carrier of heavy metal, but that organic contaminants behave in a similar manner to heavy metals, supporting the notion that resuspension is a major process in the embayment.

Fluxes of SPM show a large seasonal variation in settling rates, which is possibly related to change in water temperature

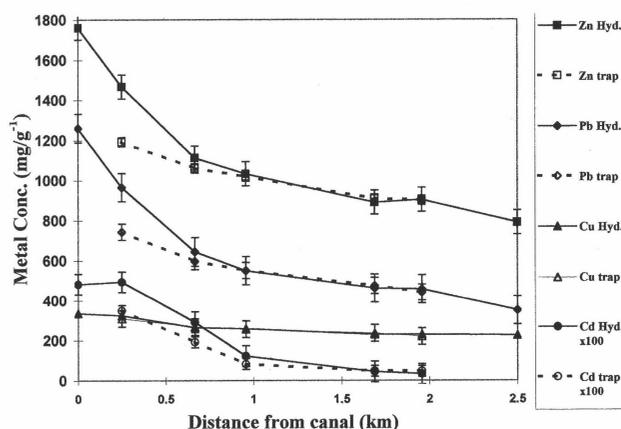


Figure 6. SPM and sediment heavy metal gradients in Iron Cove. Hydrous layer, mean of 8 samples; sediment trap, mean of 13 samples. Error bars are one SD.

(21 to 11°C) and an increase of threshold velocity required to resuspend more cohesive sediments. Other processes that could account for reduced settling rates include decreased biological activity by infauna, reduced phytoplankton production, and algal mats forming on the sediment surface during winter.

The ecological implication of resuspension is that particulate matter and associated nutrients and contaminants are continuously recycled into the water column. Highly contaminated surficial sediment in these embayments, when resuspended, is potentially available to, not only infauna, but also pelagic fauna. In addition, resuspended particles with excess potential metal-binding capability may adsorb dissolved contaminants and settle again, increasing the estuary's ability to act as an efficient sink for contaminants.

Management strategies for areas of contaminated estuarine sediment need reviewing, owing to the widespread implications of continuous cycling of potentially toxic materials in shallow water environments. Remediation options for contaminated sites include in-situ containment or excavation, treatment and remote containment (Förstner 1995).

Conclusions

Offchannel embayments in Port Jackson are highly contaminated by Cu, Pb, Zn and Cd from material emanating from stormwater canals and other localised point sources. Once deposited in these embayments, contaminants are continuously resuspended by natural processes and anthropogenic activities into the water column and are, thus, potentially available for uptake and incorporation into the food chain. Further work using high temporal resolution recording and sampling methods is being conducted to investigate processes of resuspension in these environments.

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