

Public Works Committee

Inquiry into the Impacts of the Western Harbour Tunnel and Beaches Link

Hearing 17 September 2021, Supplementary questions

Questions for Australian Marine Science Association

- 1. The Metro Southwest Business Case summary documents show that the project team chose not to use an immersed tube due to the risks to the environment being too high in a location very close by, but further East. To what extent are the Harbour problems you've identified caused by the choice to use an immersed tube method to cross the Harbour and Middle Harbour?*

We can say with certainty that the choice to use an immersed tube method for the two crossings is far more damaging to the marine environment than a bore tunnel due to disturbance of the sediments (contaminated and uncontaminated) by dredging, boating, pile driving, and other activities associated with construction. Certainly, the use of shallow silt curtains during construction which are not anchored to the seafloor will not prevent sediments from dispersing widely.

- 2. You mentioned that there was insufficient data for you to comment on Middle Harbour. Is the quantity and quality of the data in relation to Middle Harbour acceptable at this stage of the project?*

With regard to the EIS (Appendix M, Contamination, Jacobs Group) and the number of sediment cores analysed in the Golder Douglas (2017) Contaminants Report, specifically for both immersion tube tunnels (ITT), it is clear that insufficient samples of marine sediments were taken and so insufficient analyses were done.

As AMSA mentioned in our submission, the proponents of the WHT/BL project did not consult the wealth of project-independent data in many scientific publications on the sediments and environments of Sydney Harbour. In addition to the publications attached to our submission, we attach Birch et al. (2013) which has data on the sediments of Middle Harbour. Chromium contamination was found at 50 cm depth in sediment cores and were dated to 1935, the source being legacy industry. This layer of contaminants is well buried and will be mobilised by the ITT project. Storm water runoff from Flat Rock Creek is a source of contaminants. This area has been modified by an incinerator and landfill with groundwater leachate contaminating the creek.

Appendix M of the EIS states that contaminated sediments associated with the historical industrial use of the harbour and polluted stormwater runoff have been identified within Middle Harbour and The Spit and that these potentially pose a high contamination risk to construction. Examination of data for Middle Harbour sediment cores (Golder Douglas, 2017; Table A1) shows that some samples had contaminants at or approaching sediment quality guideline values (e.g., hydrocarbons, tributyltin). While these are of concern, contaminants in the Middle Harbour sediment are much lower than found in highly contaminated sites associated with the WHT/BL project (e.g., Berrys Bay). No detailed studies were carried out on water movements as to how these disturbed sediments and associated pollutants will move up and down Sydney Harbour.

As we stated in our submission, with respect to the marine environment, sediment core analyses are the most inadequate aspects of the EIS and of most concern. The quality of the sediment analysis data, in relation to the WHT/BL project is not acceptable at this stage of the project. Based on the poor information on contaminated sediments and disturbance risk the EIS should be redone.

With respect to marine animals – a search of the archives and records at the Australian Museum shows that the Middle Harbour area is poorly studied.

3. *We have heard that two catchments are being disturbed and are contaminated (Willoughby Creek and Flat Rock Creek catchments) that feed into Middle Harbour. Do you have concerns about this?*

AMSA's scope of expertise is the marine environment. Willoughby Creek and Flat Rock Creek catchments are land-based habitats. Contamination from storm water runoff from these sites is a concern (Birch et al., 2013). Flat Rock Creek, a waterfall-gully system, was an unregulated tip and incinerator site for industrial and domestic waste from 1940-1985 and had industries nearby (refrigerator factory). The results of Birch et al., (2013) indicate that this history impacts the flow of contaminants into Middle Harbour. As this area is proposed to be a construction support site this is of concern as high risk to contaminate the marine environment. It is sensible to avoid disturbance of any industrial tip site where there is no record of what was dumped there.

Due to limited sampling and lack of rigour in the approach to replication and analysis, the data are insufficient to assess this risk.

4. *In your experience do contaminants in catchment areas have a risk of mobilisation into waterways if disturbed?*

With respect to mobilisation of contaminants from disturbed sediments, this is almost certain and is well-documented in the scientific literature.

- a. *How would you classify that risk?*

High

- b. *Would you say contamination in large catchment areas is easy and therefore inexpensive to mitigate or difficult and therefore expensive?*

We do not know what "easy" means in this question. What we can say is that contamination of a large area of Sydney Harbour from the ITT constructions is highly likely and that as some contaminants are persistent pollutants that will remain toxic for 100's of years. Thus, some chemicals cannot be mitigated and so would have to be removed and treated on land as done for sediments around the Homebush Olympic site. We believe that this is a costly undertaking.

5. *Do you think a known industrial tip site within a major catchment to Middle Harbour should be used as a dive site?*

The tip site at Flat Rock Creek is registered as contaminated land. As detailed above we suggest that disturbance of this site should be avoided.

- a. *Would it be more cost effective to avoid the use of this site?*

As we are not construction engineers, we cannot answer this question.

6. *We have heard that Middle Harbour is well recognised as a sensitive area and a nursery for Sydney Harbour in terms of wildlife – can you expand on how Middle Harbour supports Sydney Harbour and its importance to the overall ecosystem health of the Harbour?*

AMSA's brief is the marine environment and so our response is in relation to marine wildlife (birds and mammals). We are not aware that Middle Harbour is well recognised as a sensitive area and a nursery for Sydney Harbour in terms of marine wildlife, although upstream of the site there are extensive mangroves which are known to be important nursery grounds. As mentioned above, this area is poorly studied in the scientific literature. According to the WEPA submission Little Blue Penguins are common in the area and this seems likely as this area is close to the rookery at Collins Flat, Manly.

7. *Middle Harbour is due to be dredged at a point where contaminants have been identified (including PFAS) and contaminated sediment will be barged out under the Spit Bridge into the main Harbour. Are you concerned about the dredging and potential of spill in Middle Harbour and near the Northern Beaches?*

Damage to the marine environment through dispersal of contaminated sediment is of great concern. During barge transport of contaminated sediments there is a risk for spill. This is a major concern for the WHT/BL project. We do not have data to assess particular risk to the Northern Beaches.

8. *The EIS states that contaminated sediment will need to be dried out at an unknown location. Are there risks associated with drying out contaminated sediment to surrounding ecosystems and residents?*

Yes – dried contaminated sediments can be readily transported as aerosols with high risk to surrounding ecosystems and residents. This is particularly the case for the WHT/BL project as carcinogenic and poisonous contaminants occur in sediments at both the ITT sites and construction support sites (e.g., dioxins, tributyltin, chrome, arsenic, mercury). Humans breathing in these toxics would have adverse health impacts. These chemicals and their mixtures are highly damaging to the marine environment.

9. *A large amount of waste has been earmarked as suitable for “offshore disposal” (in total, 1,450,000 tonnes). Do you have concerns about this?*

Yes, absolutely. The EIS did not sufficiently document the location and depth of the contaminants – the number of samples taken was highly inadequate. We do not have a sufficient understanding of where the contaminants are. As Dr Ryall stated in his submission there are 18 sites that are likely to be contaminated for which there are no samples analysed.

The WHT the corridor was moved to the north, but only a few extra sediment cores were analysed. The proponents were required to analyse more sediment samples for the Commonwealth in the context of offshore disposal, as stated in the submission report, but these data are not available. For the marine environment offshore disposal is one of the most hazardous and uncertain issues of the WHT/BL project and needs urgent attention. Dr Ryall's submission indicated that the EIS overestimated the amount of contaminated spoil. This aspect of the EIS should be revisited in detail.

10. *Are you aware of the decline of Little Penguins in the Harbour?*

Yes, prevailing evidence suggests that this is largely due to disturbance of the burrows by domestic dogs.

a. *How do you think the increased marine traffic required to support the immersed tube works could affect them and the other 21 threatened or endangered marine species identified in the EIS?*

We are not clear on the 21 species. The appendices in the EIS Biodiversity chapter (Chapter 19, Cardo Consultants) name 23 (Appendix A Threatened Species) and 30 Appendix C Protected Species) species. However, many of the species named in the appendices are rarely/never seen in Sydney Harbour and so these appendices are off base (e.g., Tropical species:– Hawksbill Turtle, Leatherback Turtle, Green Turtle, Loggerhead Turtle, sea snake, Dugong, Offshore/Oceanic species: Southern Right Whale, Humpback Whale, Blue Whale, Whale Shark).

It would have been expected for the EIS to focus on marine species that are of concern in Sydney Harbour and thus have a high risk of being affected by the WHT/BL project. These include Whites Sea Horse, *Posidonia* sea grass, New Zealand Fur Seal, Little Blue Penguin and several pipefish species. We note that the endangered soft coral *Dendronephthya australis* is not mentioned.

What is missing from the EIS is a considered and robust risk assessment for the vulnerable species that we know use Sydney Harbour as a key habitat.

11. *Do you think that safe swimming at Dawn Fraser Baths, Greenwich Baths, MacCallum Pool, Cremorne, Northbridge Baths, Clontarf Baths and Manly Dam will be able to be guaranteed during the 8 year construction program?*

The corridor of the WHT is a highly hydrodynamic crossing and so there is a high risk that sediment and contaminant dispersal will be a risk to safe swimming at Dawn Fraser Baths and Greenwich Baths cannot be guaranteed. The WHT ITT has very a high potential to release toxic chemical mixtures into the water. The EIS did not provide sufficient data on water circulation for AMSA to understand the transport of contaminants to all of these swimming facilities.

12. *What type of monitoring would be needed to alert the community to dangerous levels of contamination including heavy metals, PFAS and other contaminants?*

With respect to risk to human and environmental health water samples would have to be collected daily for analysis of contaminants. As some contaminants are toxic at very low concentrations toxicity is determined using standard marine ecotoxicology testing.

- a. *Does such detailed, real time monitoring exist?*

Yes – in these monitoring programs water samples are delivered to accredited laboratories (e.g., Australian Government Analytical Labs, Ecotoxicology Labs) promptly after collection for rapid testing and reporting as done for water sample analysis during the remediation of areas around Homebush for the Sydney Olympics.

13. *What are the climate associated impacts of destroying or damaging mangrove and sea kelp areas?*

Mangroves and kelp are very important as a source of blue carbon – major sinks for CO₂. For the same reason that deforestation is a concern on the land destruction of mangrove and kelp has climate change impacts with regard to CO₂ sequestration. Another important, but less appreciated service that mangrove and kelp provide is buffering the environment from ocean acidification. By taking up CO₂ and releasing the products of photosynthesis (e.g., oxygen) these plants protect marine species, in particular species such as oysters that make a shell.

Reference: Birch et al. (2013) The use of vintage surficial sediment data and sedimentary cores to determine past and future trends in estuarine metal concentrations (Sydney estuary, Australia). *Science of the Total Environment* 454-455: 542-561.



The use of vintage surficial sediment data and sedimentary cores to determine past and future trends in estuarine metal contamination (Sydney estuary, Australia)

G.F. Birch ^{*}, C.-H. Chang, J.-H. Lee, L.J. Churchill

Environmental Geology Group, School of Geosciences, The University of Sydney, Sydney, New South Wales, 2006, Australia

HIGHLIGHTS

- Multiple vintages of surficial sediment metal data provide past and future contamination trends.
- Sedimentary metal concentrations are declining in the upper and central in Sydney estuaries.
- Declining sediment metal levels due to reduction of industry and introduction of regulation
- Major present-day source of sedimentary metals in Sydney estuary is stormwater.
- Modelled relaxation rates are optimistic due to high metal stormwater concentrations.

ARTICLE INFO

Article history:

Received 27 July 2012

Received in revised form 25 February 2013

Accepted 25 February 2013

Available online xxx

Keywords:

Metals
Surficial sediment
Estuary
Relaxation rate
Sydney estuary

ABSTRACT

The objectives of the present investigation were to determine past trends in sediment contamination and possibly predict future trends. Multiple vintages of surficial sediment metal data, from a quasi-decadal 'Status and Trends' programme, were used to provide large-scale spatial information on current status and temporal change. This information was augmented by sediment cores, specifically located to verify surface sediment data and to determine trends at major points of stormwater discharge. The data obtained indicate that surficial sediment metal concentrations have declined, since about the early 1990s, in extensive parts of the upper and central estuaries and have increased slightly in the lower estuary, due mainly to a down-estuary shift in industry and urbanisation. Declining surficial sediment metal concentrations is due to a movement of industry out of the catchment, especially from foreshore areas and the introduction of regulation, which prevent pollutants being discharged directly to the estuary. The major present-day source of metals is stormwater, with minor inputs from the main estuary channel into embayments and runoff from previously contaminated mainland sites. Modelled relaxation rates are optimistic as high metal concentrations in stormwater will slow predicted rates. Stormwater remediation should be the main managerial focus for this estuary. Multiple vintages of surficial sediment metal data covering the past 30 years, supplemented by sedimentary core data, have allowed past and future contamination trends to be determined. This type of science-based information provides an important tool for strategic management of this iconic waterway.

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1. Introduction

Sydney estuary (Australia) has considerable environmental, economic, recreational and aesthetic value. However, the system has had to endure considerable stress due to extensive urbanisation and industrialization for more than a century. To maintain the health of such an ecosystem requires a balance between protection and use of the estuary and catchment through coordinated management (Birch, 2007). In recent years, science-based environmental indicators, which describe complex interactions between natural and human systems, in simplified terms, have become a central element

of resource management (Rice, 2003). The challenge is to choose a set of indicators that may be used in a 'weight-of-evidence' approach and which will provide management with information in a less complex fashion for decision-making and planning (Rice, 2003). Sedimentary metals provide an indicator of contaminant-related biological stress and are an easy and inexpensive approach to measure the quality of an aquatic system (Chatterjee et al., 2007). Sediments integrate contaminants over time and faithfully record the history of chemical condition. Sediments are also the only indicator to provide quantitative information on the pristine condition and specifically, the human component of environmental change (Birch and Olmos, 2008).

Sydney estuary, in central New South Wales, Australia, is one of the most beautiful in the world, and is home to about 4.5 million people (Birch, 2007). The catchment (500 km²) is highly industrialised

^{*} Corresponding author. Tel.: +61 2 93512921.

E-mail address: gavin.birch@sydney.edu.au (G.F. Birch).

and urbanised (86%) (Birch et al., 1996; Birch et al., 1999), whilst the estuary (30 km long, up to 3 km wide and 50 km²) is a well-mixed (Hatje et al., 2001; Lee et al., 2011), dendritic drowned-river valley (Roy, 1983). Sediments in the estuary are subject to significant contamination by metals (Birch and Taylor, 1999), nutrients (Birch et al., 1996), polycyclic aromatic hydrocarbons (McCready et al., 2000, 2003) and organochlorine compounds (Birch and Taylor, 2000, 2002) and is classified as “severely modified” by the National Audit of estuaries (NLWRA) (OzCoast, 2000; NLWRA, 2002).

Sydney estuary is a mesotidal system with a maximum tidal range of 2.1 m (Lee and Birch, 2012). Water circulation in Sydney estuary is controlled by estuary morphology/bathymetry and tidal currents. Typically, surface currents are 0.3 to 0.5 m/s, but bottom currents are considerably lower (1–30 cm/s) (Irvine, 1980). Estimates of flushing times vary depending on the rainfall event and location in the waterway. Typical flushing times are of the order of 5 to 10 days, however in the upper reaches of the waterway times may be as long as 130 days and for major flooding events the estuary may take up to 7 months for complete flushing in upstream sites (Das et al., 2000). A low density (~1.2 kg/m³), readily resuspended layer up to 3 cm thick (mean thickness ~1.3 cm) covers approximately 67% of the estuary floor (Irvine, 1980). Near-bottom currents > 30 cm/s are capable of resuspending sediment from this layer into the water column along the main estuary channel (Irvine, 1980), whilst some material is escaping offchannel embayments (Lee, 2012).

The current investigation is of six major embayments of Sydney estuary, i.e., Blackwattle and Rozelle Bay, Iron Cove, Hen and Chicken Bay, Homebush Bay, Lane Cove and Middle Harbour (Fig. 1). Catchment size varies from 9507 ha (Lane Cove) to 771 ha (Hen and Chicken Bay) (Table 1). The largest catchment land-use is residential (35–55%), followed by roads (13–30%) and industrial/commercial (4–20%), whereas parkland comprises 6–28% of land-use. Blackwattle and

Rozelle Bays, being close to the location of the first settlement, were impacted early by industry. However, much of the heavy industry along the dockyards has been replaced with parkland and residential areas. Iron Cove catchment is intensely urbanised (55%) (Birch and McCready, 2009) and inter-tidal areas have been extensively reclaimed with estuarine sediment and fly ash (Sabolch, 2006; Birch and McCready, 2009). Hen and Chicken Bay catchment is also extensively urbanised (57%) and the entire shoreline has been reclaimed (Birch et al., 2009). Sediment in Homebush Bay contains high concentrations of dioxins and other organic chemicals (DDT) (Birch et al., 2007; Birch and O’Hea, 2007) and fishing is banned for public health reasons. Reclamation has removed wetland habitats and severely reduced salt marsh areas (McLoughlin, 2000). Lane Cove and Middle Harbour catchments comprise mainly residential (54% and 53%, respectively) and substantial parkland (24% and 18%, respectively).

The ‘Status and Trends Programme’ of the Environmental Geology Group at Sydney University has collected surficial sediment contaminant data at approximately decadal intervals since 1977. The objective of the current study was to use these sedimentary metal data sets to investigate human-induced change in six major embayments of Sydney estuary. A further objective was to model future projections of sediment quality using these historical trends. This study provides important information for the management of this iconic water way. The possible biological risks associated with metal concentrations as observed in these sediments are the subject of a future manuscript.

2. Methodology

2.1. Sample collection

Surficial sediment and core samples have been taken in Sydney estuary over the last 30 years, beginning in the late 1970s (Irvine, 1980)

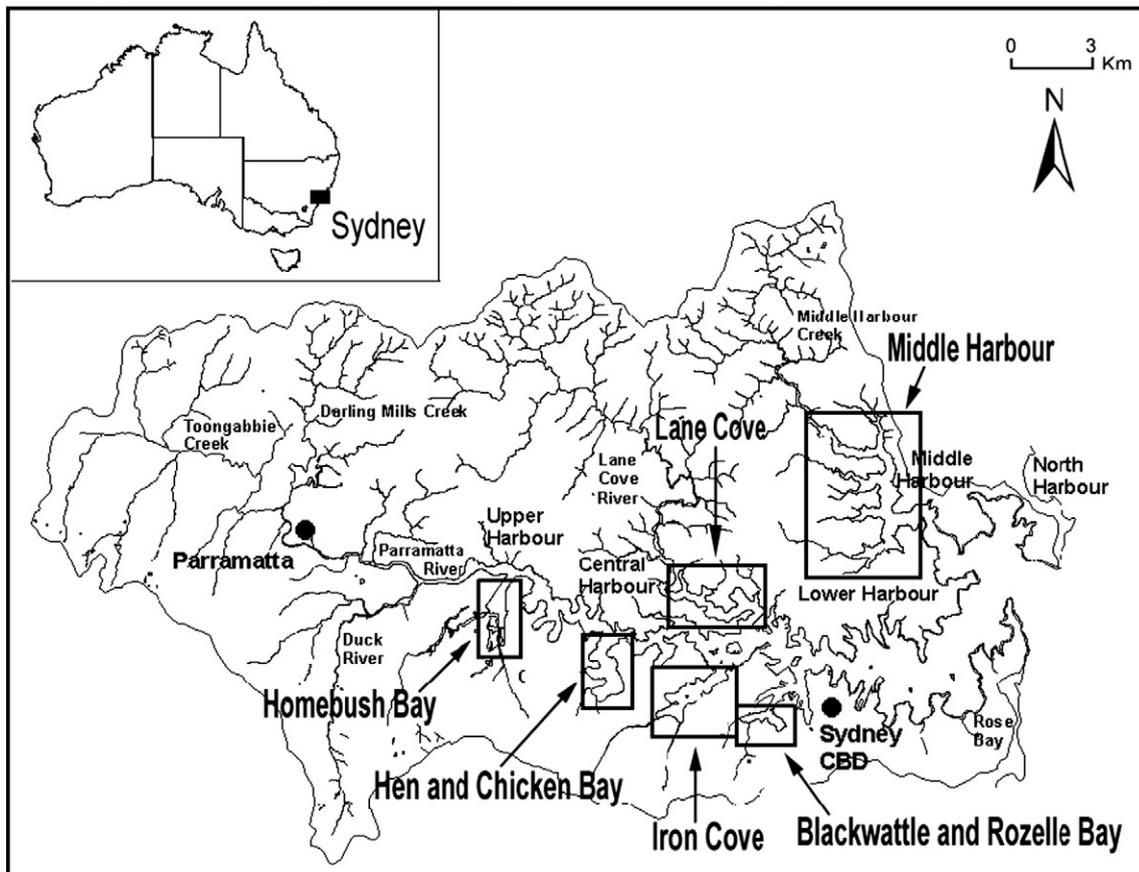


Fig. 1. Location of study areas.

Table 1
Catchment landuse areas and sub-estuary area (ha).

Bay	Catchment									Sub-estuary
	Residential	Commercial	Rail	Education	Parkland	Industrial	Road	Hospital	Total	
BW/RZ Bay	618.5	322.6	52.2	83.7	113.6	30.6	518.1	1.0	1740.3	212.0
Iron Cove	1009.9	114.4	25.5	95.7	151.8	20.5	411.7	16.8	1846.5	163.0
H & C Bay	393.4	40.8	4.7	18.0	138.5	11.0	164.4	0.2	771.0	175.0
Homebush B	1180.1	65.9	74.7	68.4	857.9	308.4	482.3	1.9	3039.6	88.0
Lane Cove	5142.9	141.3	27.3	399.9	2271.3	238.2	1211.1	75.0	9507.1	272.0
Central M H	1547.0	60.0	6.1	56.9	535.5	236.3	487.1	3.8	2932.6	397.0

BW—Blackwattle, RZ—Rozelle, H & C B—Hen and Chicken Bay, M H—Middle Harbour.

and most recently in 2010 (current study). Sydney estuary was divided into areas (strata) based on sediment characteristics (Irvine, 1980) and samples were taken randomly within each stratum (Birch et al., 2008a, 2008b). The surficial sediment data used in the current work were collected in Rozelle Bay/Blackwattle Bay in 2010 (Chang, 2011) (n = 35); Iron Cove in 2000 (Hutson, 2005) (n = 46) and 2009 (Chang, 2009) (n = 45); Hen and Chicken Bay in 2004 (King, 2004) and 2010, (Chang, 2011) (n = 45); Homebush Bay in 2004 (King, 2004; Hutson, 2005) (n = 31) and 2010 (Chang, 2011) (n = 30); Lane Cove in 1999 (LCEC, 1999) (n = 63) and 2010 (Lee, 2011) (n = 30); and Middle Harbour in 1999 (Fanous, 1996) (n = 119) and 2010 (Churchill, 2011) (n = 42).

All samples used in the current study were recovered and analysed in the same manner. Surficial sediment was taken using a stainless steel box-corer and the upper 1 cm was removed, placed in a plastic bag and stored at 4 °C until laboratory analysis, with air excluded to reduce chemical reactions. Cores were taken in the same locations as previously for dated cores (Taylor et al., 2004) to provide more recent information (2000 to 2010) and in selected areas to verify the results of the surficial sediment data. Two types of vertical core were collected. High-resolution, short (<1.5 m) push cores were taken with a polycarbonate barrel, sub-sampled at 1 cm intervals up to 10 cm sediment depth and then at 2 cm intervals to the bottom of the core to record recent, subtle changes in metal concentrations. A 6-meter long PVC core barrel was used to penetrate pre-anthropogenic sediment to obtain 'background' metal data. These cores were cut in half, logged (sediment attributes recorded) in the laboratory and samples were taken from each sedimentary layer, i.e. sampling was based on the micro-stratigraphy. Sub-samples from cores were stored in a similar manner to surficial samples. Sampling locations were determined using a hand-held Geographical Positioning System (GPS) (Fig. 2), imported into ArcMap using the GCS_WGS_1984 coordination system (EOSAN, 1998) and transformed into shape files.

2.2. Laboratory analysis

Normalisation of sedimentary metal data was applied to reduce the confounding effects of variable grain size, to ensure spatial and temporal data comparability and to provide valuable information on pollutant dispersion and source (Grant and Middleton, 1990; Loring, 1991; Szava-Kovats, 2008; Matthai and Birch, 2001; Birch, 2003; Mudge et al., 2003; Birch et al., 2008a, 2008b). Size normalisation was conducted by wet-sieving through a 62.5 µm nylon mesh using deionised water. The fine fraction and total sediment were also analysed for a suite of six metals (Cu, Pb, Zn, Ni, Co and Cr) by aqua regia digestion (3 mL concentrated HCl + 1 mL concentrated HNO₃ + 10 mL ultra pure 18.2 mΩ water) and heated at 120 °C for 2 h (modified USEPA 200.8 Rev 4.4 method) (US EPA, 1994). The solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). A reference material (AGAL-10) and blank were included in each analytical batch of 20 samples. A quadruplicate sample was run every 40 samples to test the precision of extraction and degree of small-scale spatial variance in the field. Concentrations were provided as dry weight.

2.3. Data quality

Accuracy of chemical analyses was determined by repeated (n = 55) analysis of an International Reference Material (IRM) (AGAL-10) and expressed as recovery, which was between 95% and 110% for Cu, Pb, Zn, Co and Cr and was 116% for Ni. Mean values for all metals were within the recommended values for the IRM, except Zn which exceeded this value by 2.79 mg/kg. Precision, determined from the IRM and expressed as Relative Standard Deviation, was <5% for all metals. Zinc was the only metal that exceeded detection limits in blanks for some samples and this value (0.17 mg/kg) was deducted from sample metal concentrations.

2.4. Background metal concentrations and magnitude of anthropogenic change

The impact of human influence on the estuarine environment was determined using grain-size normalised (<62.5 µm) sedimentary metal data (Forstner and Wittmann, 1979) obtained from long cores taken in undisturbed areas of deposition in the estuary (Birch, 2003; Birch and Olmos, 2008; Olmos and Birch, 2010). The magnitude and spatial extent of human-induced change was determined by expressing surficial metal concentrations as enrichment over background levels observed at pre-anthropogenic sediment depths (Carballeira et al., 2000; Birch, 2003; Mudge et al., 2003; Birch et al., 2008a, 2008b). This section of the sediment profile has been shown to be pre-industrial and deposited before early settlement, using dated cores from Sydney estuary (Taylor, 2000; Taylor et al., 2004) and in cores from other estuaries (Zwolsman et al., 1996; Deely and Fergusson, 1994; Olmos and Birch, 2010). Core data should be used with caution as subsurface sediments may be re-mobilized by biological (Luoma and Phillips, 1988; Geyh and Schleider, 1990) and physical/chemical processes (Ridgway and Price, 1987; Benoit and Hemond, 1991). However, the depth of re-mobilization in the reducing, organic-rich sediment of Sydney estuary (Taylor et al., 2004) (Koide et al., 1973; Mayer, 1994) has been shown to be restricted to the upper few centimetres (Simpson et al., 2002).

A two-times standard deviation of the mean background concentration for any metal equated to an enrichment factor of about 1.5 times, which was thus considered indicative of initial human influence (the same value as used by Roussiez et al., 2006 and Roussiez et al., in press). Enrichment factors of 1.5–3, 3–5, 5–10 and > 10 times were classified as minor, moderate, severe and very severe modification, respectively (Birch and Olmos, 2008). A Mean Enrichment Quotient (MEQ) was calculated by summing EFs for Cu, Pb and Zn and dividing by three to provide an 'average' magnitude of human-induced change expressed by the three metals (Birch and Olmos, 2008; Olmos and Birch, 2010).

2.5. Predictive modelling of human-induced change

Spatial interpolation of contaminant data was performed by Ordinary Kriging Prediction, a Geostatistical Analysis function available in ArcGIS Version 10 (ESRI, 2009) and results were exported to raster

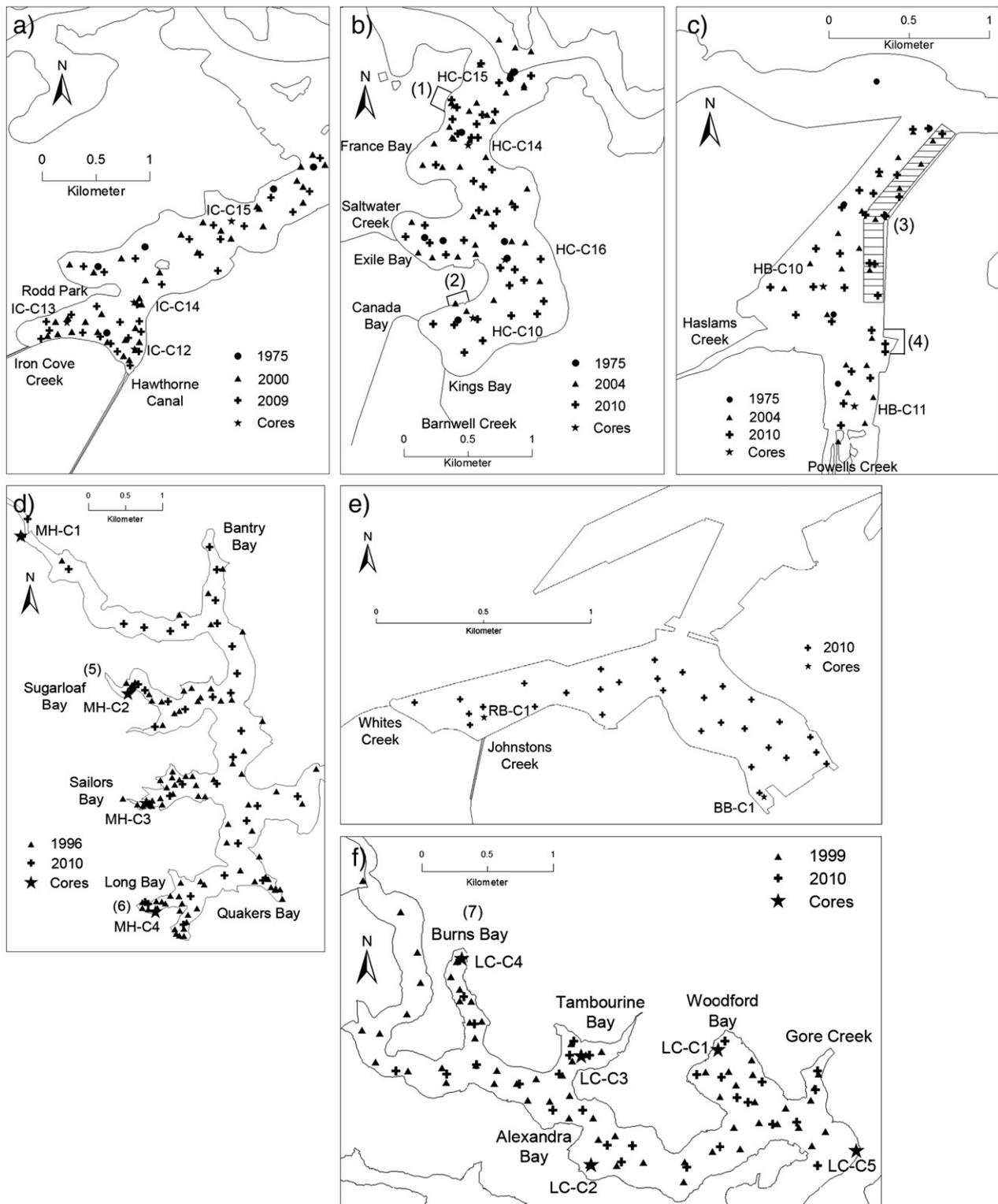


Fig. 2. Sample locations. (a) Blackwattle and Rozelle Bays, (b) Iron Cove, (c) Hen and Chicken Bay, (d) Homebush Bay, (e) Lane Cove, and (f) Middle Harbour. Locations mentioned in the text: 1. British–Australia Lead Manufacturers Pty. Ltd. (BALM), 2. Australia Bronze Crane Copper Ltd. (Austral Bronze), 3. Remedial footprint, 4. Berger Paint factory, 5. Pioneer Tannery, 6. James Forsyth Rosewall tannery and others, 7. Flat Rock Creek (Gully) and tip, Walter Burley Griffin Incinerator, Naremburn Waterfall.

graphics. The Raster Calculator in the Spatial Analyst tool was used to calculate temporal change of surficial sediment metal distributions between vintages of datasets by arithmetic subtraction of raster layers (ESRI, 2009). Sample density was increased from approximately one sample/4–8 ha in regions of regular surficial concentrations to 1 sample/ha in areas of rapid spatial change to provide detailed metal distributions using the Ordinary Kriging Prediction function.

Predictive modelling was undertaken to estimate future surficial sediment metal (Cu, Pb and Zn) concentrations using two approaches. Firstly, the relaxation rate (mg/kg/yr) was determined using the Raster Calculator tool (ArcGIS Spatial Analyst) to subtract one raster layer from the other and then divide by the interval (in years) between surveys (ESRI, 2009). Predicting 2020 spatial distributions of sedimentary metals used these annualized relaxation rates, multiplied by ten and

added to the 2010 maps (Olmos and Birch, 2010). The second method used declining metal concentrations near the top of cores taken in the present study. Trendlines were used to calculate the number of years metal concentrations may take to reach values that are twice the background level (Fig. 3). Sedimentation rates were determined from a previous study, undertaken at similar coring locations to the present investigation (Taylor et al., 2004). Results of the two approaches were compared to confirm outcomes. Predictive modelling assumed activities in the catchment (supply) and dispersion processes within the estuary that remained constant over the period of investigation.

3. Results

All surficial sediment metal concentrations are normalised (fine-fraction values).

3.1. Rozelle and Blackwattle Bays

Results from the 2010 survey showed that surficial sediment mantling these bays was generally mud (>50% 62.5 μ material) (75–99%) with >50% sand adjacent to two creeks entering Rozelle Bay (Whites and Johnstons Creeks). Surficial sediment Cu, Co and Zn concentrations were highest adjacent to Whites Creek, whereas Cr, Pb and Ni were highest at the mouth of Johnsons Creek (Fig. 4i & j).

Data collected in 1994 in Rozelle and Blackwattle Bays were insufficient to determine temporal changes over the intervening period using surficial sediment. The short, high-resolution and deep cores taken in Blackwattle Bay (BB-C1) showed onset of metal contamination at 75 cm sediment depth and maximum concentrations for all metals at

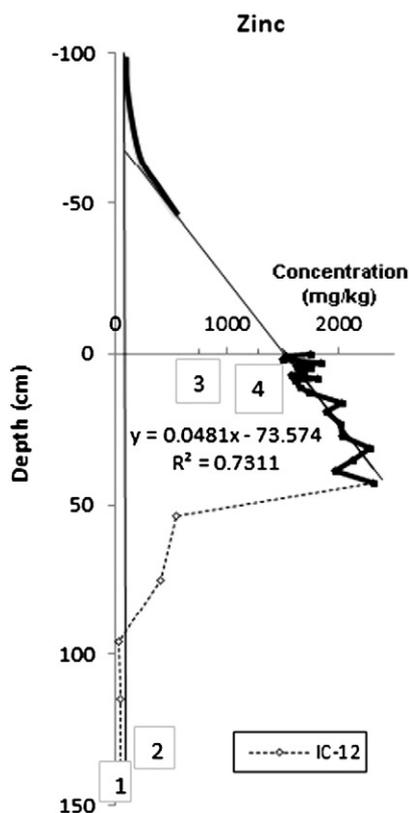


Fig. 3. Estimation of pre-anthropogenic (background) concentration and time taken to reduce surficial concentrations to twice background levels. Straight line projection and more likely progressive declining concentration trend. Figure notation: 1. Samples at background concentrations at the base of the core, 2. Background trend line, 3 & 4. Fluvial particulate Zn concentrations discharged into Iron Cove from Hawthorne Canal and Iron Cove Creek, respectively.

22 cm with strong declining trends to the surface (Fig. 5a–d). In Rozelle Bay (RB-C1), maximum concentrations were at 80 cm sediment depth and only Co, Cr and Ni were at background levels at the bottom of the core (142 cm).

3.2. Iron Cove

The 2009 survey showed Iron Cove to be mantled in mud (>95%), however adjacent to Iron Cove Creek, surficial sediment was sandy (>70% sand). Concentrations of Cu, Pb, Zn and Ni were higher adjacent to inlets of Iron Cove Creek and Hawthorne Canal and gradually decreased towards the bay mouth (Fig. 4a & b). In contrast, Co and Cr concentrations decreased from the bay mouth towards the headwaters.

Although there was a general decline in metal surficial sediment concentrations from 1977 to 2000 over most of Iron Cove, sediments adjacent to the two inlets exhibited an increase in Cu, Pb and Zn concentrations by approximately 140 mg/kg, 270 mg/kg and 1167 mg/kg, respectively over this period. Nickel and Co decreased throughout Iron Cove during this time, whereas Cr increased markedly at the bay mouth adjacent to the main channel of the estuary.

Generally, surficial sediment metal concentrations decreased from 2000 to 2009 in the majority of Iron Cove, but Cu and Zn increased adjacent to the Iron Cove Creek and Hawthorne Canal. Nickel and Co concentrations remained constant over this period and Cr increased, especially at the mouth of the embayment. Lead concentrations declined, except adjacent to the eastern shore (Fig. 6a).

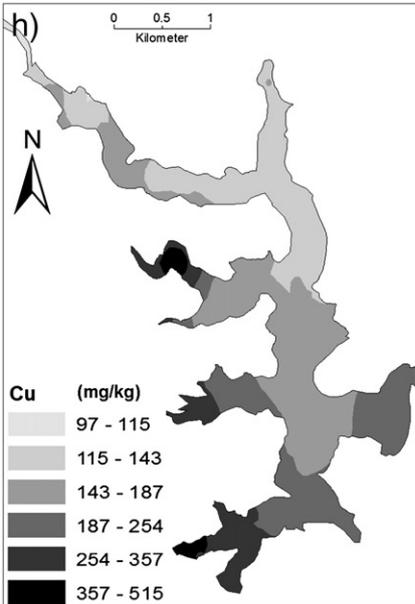
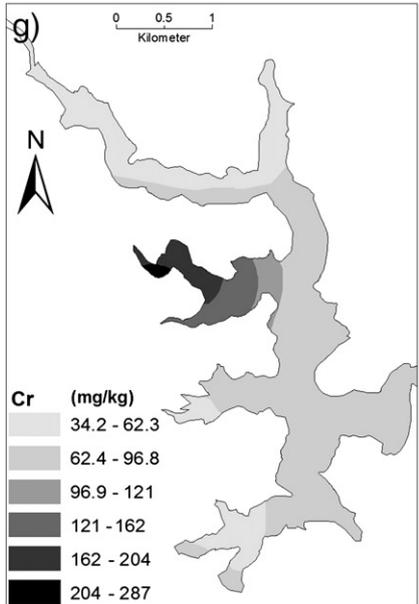
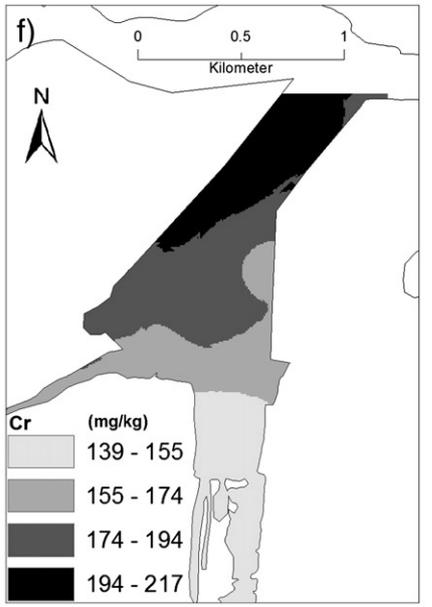
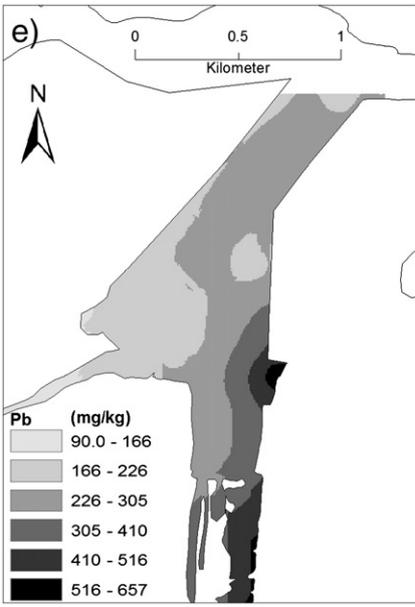
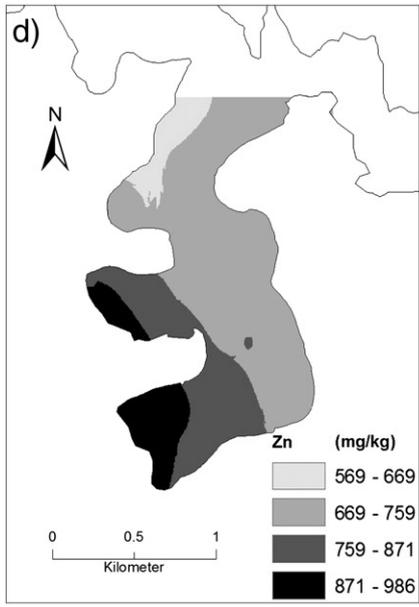
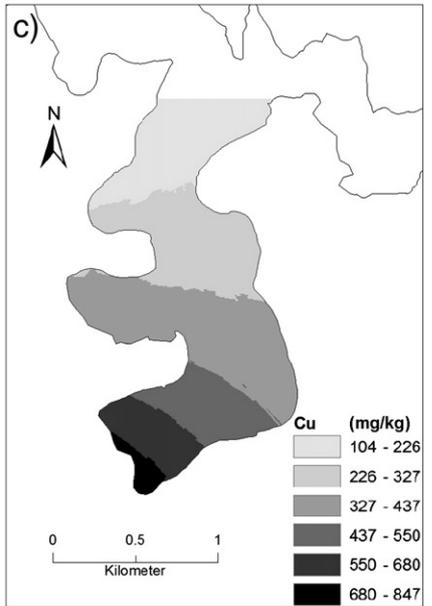
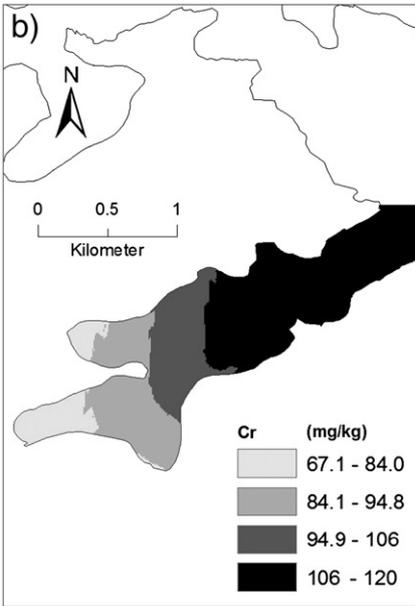
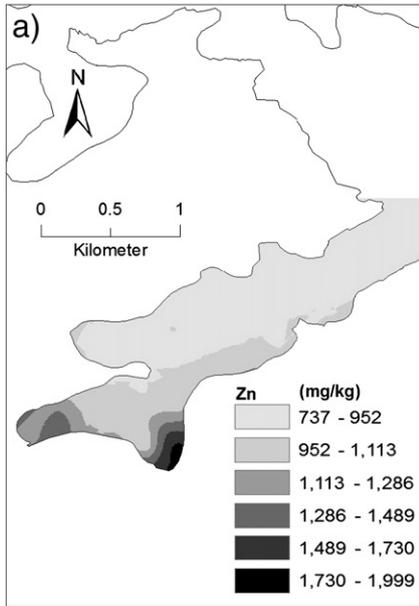
The core (IC-C12) located at Hawthorne Canal inlet (Fig. 5a–d) displayed strong decreasing trends in Pb and Zn towards the top of the core, whilst the concentration of other metals remained constant, or declined marginally. The onset of contamination was at 95 cm sediment depth and maximum concentrations were at 40 cm. Cores (IC-C13 and C14) located at the mouth of Iron Cove Creek and south of Rodd Island, respectively, were influenced by dredging and are not presented. However, the upper profiles were similar to the core (IC-C12) at the mouth of Hawthorne Canal. Core (IC-C15) taken near the bay mouth displayed decreasing down-hole trends in Cr, Cu, Pb and Zn concentrations.

3.3. Hen and Chicken Bay

Sampling in 2010 showed surficial sediments covering Hen and Chicken Bay to be muddy (>85%), except in Exile and Kings Bays (<25% mud). Copper and Cr were most concentrated (750 mg/kg) in sediment at Barnwell Creek mouth in Kings Bay and steadily decreased towards the bay mouth (approximately 150 mg/kg) (Fig. 4c & d). Lead, Zn and Ni concentrations were highest adjacent to the creeks entering Canada Bay (Cintra and Barnwell Creeks) and Exile Bay (Saltwater Creek) and Co concentrations were consistent across the bay.

Sparse surficial sediment data in 1977 in Hen and Chicken Bay rendered interpretation of temporal trends problematic for the period 1977 to 2001, although a general decline in Cu, Pb, Zn and Cr concentrations was evident for the entire bay and most strongly in the south west. Surficial sediment metal concentrations declined marginally during the period 2001 to 2004 in the majority of the Bay. Between 2004 and 2010 surficial sediment Cr, Cu, Ni and Pb concentrations decreased by approximately 4 to 40 mg/kg; 20 to 200 mg/kg; 0.5 to 4.5 mg/kg and 20 to 180 mg/kg, respectively (Fig. 6b). Surficial sediment Zn concentrations increased immediately adjacent to the three stormwater inlets into Hen and Chicken Bay, however these patterns were not verified by core data.

Metal concentrations in sediment in the uppermost section of the four cores taken across Hen and Chicken Bay showed declining trends. Two cores located in the southern bay (HC-C10 and C16) displayed a minor increase in metal concentrations at approximately 50 cm sediment depth and reached a maximum at about 10 cm, which was similar in the central bay (HC-C14). A core located



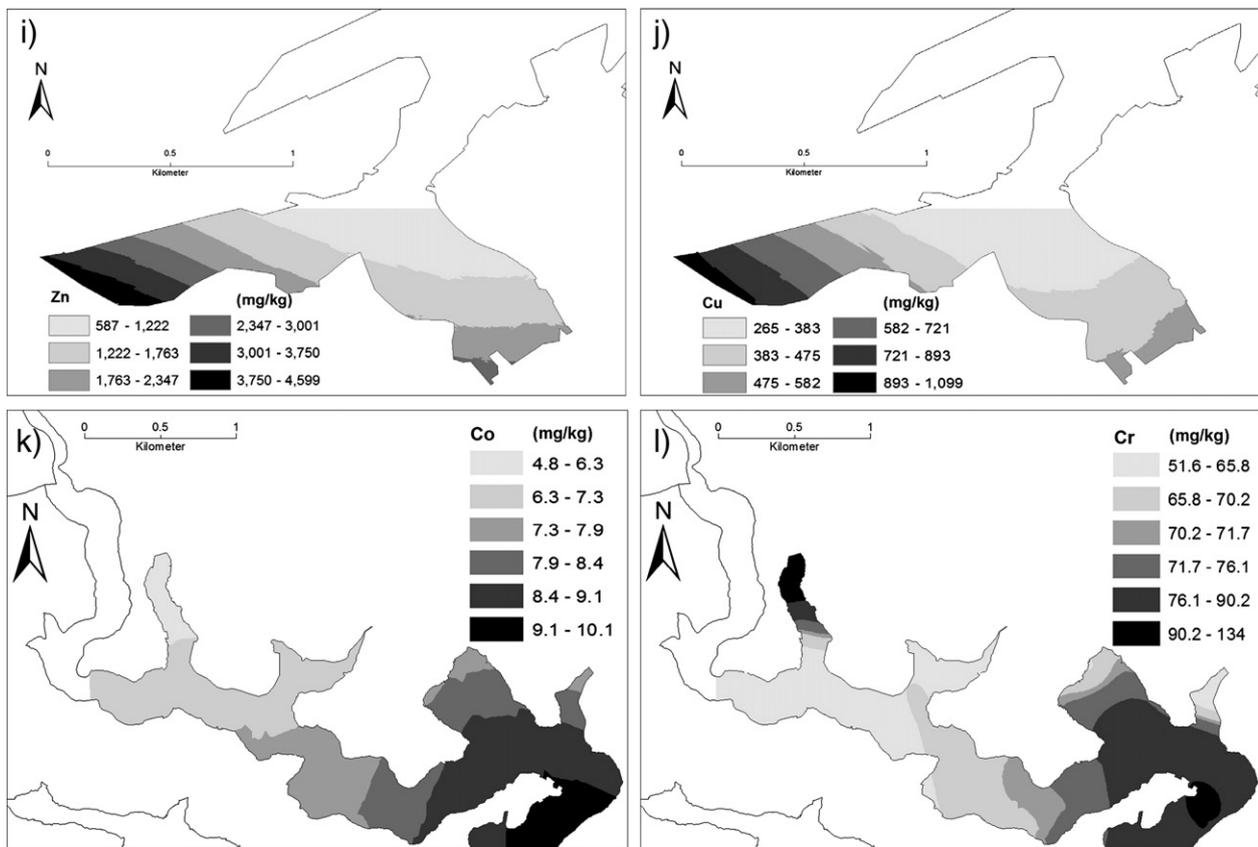


Fig. 4. Surficial sediment metal concentrations. (a) Zinc and (b) Cr in Iron Cove; (c) Cu and (d) Zn in Hen and Chicken Bay; (e) Pb and (f) Cr in Homebush Bay; (g) Cr and (h) Cu in Middle Harbour; (i) Zn and (j) Cu in Blackwattle/Rozelle Bay; and (k) Co and (l) Cr in Lane Cove.

adjacent to the northwest coast of the bay (HC-C15) contained sediment with unusually high Pb concentrations (1200 mg/kg) for this bay at approximately 40–60 cm sediment depth, which decreased rapidly to the surface (Fig. 5a–d). All cores reached background concentrations for all metals at between 50 and 60 cm sediment depth, except for core HC-C15, which did not penetrate pre-anthropogenic levels.

3.4. Homebush Bay

Results of the 2010 survey indicated that surficial sediments in Homebush Bay were muddy (mud >85%), except for the recently dredged north eastern shore, which is now mantled in recently deposited gravels. Metals in sediment covering Homebush Bay exhibited four distinct distribution patterns. Concentrations of Cu and Zn declined rapidly with distance from Powell Creek inlet, whereas concentrations of Pb and Ni were highest in a small embayment on the south east coast (Fig. 4e & f). High concentrations of Cr in sediment at the mouth of Homebush Bay decreased rapidly towards the headwaters of the embayment and Co was most enriched adjacent to the central eastern coastline.

Copper, Cr, Co, Ni, Pb and Zn concentrations decreased in surficial sediments in most of Homebush Bay between 1977 and 2004 and Pb increased in a small concave on the mid-east shore. Zinc and Cr increased in concentration adjacent to Powell Creek.

In the period 2004 to 2010 Ni, Pb and Zn increased in surficial sediments near a small concave on the mid-east coast and declined in the remainder of the bay, along with Cu, Co and Cr (Fig. 6c). Copper concentrations in surficial sediment adjacent to Haslams Creek increased by about 35 mg/kg during this time.

A core (HB-C10) taken in the central bay recorded background concentrations for all metals at 50 cm sediment depth and concentrations

increased up to 12 cm sediment depth, before declining to the top of the core (Fig. 5a–d). Chrome concentrations were substantially elevated (380 mg/kg) at 12 cm sediment depth. Subsurface sediment concentrations displayed a similar distribution to a core taken in the south east bay area adjacent to Powells Creek (HB-C11), except that Cr and Zn concentrations increased to the top of the core.

3.5. Lane Cove

The majority of sediments mantling Lane Cove estuary in the 2010 survey were muddy (>70% mud) with the exception of sediments in Woodford Bay and the upper central channel (<50% mud). Cobalt, Pb and Zn concentrations were highest towards the mouth of the Lane Cove estuary (Fig. 4k & l), whereas Cr and Cu concentrations were enriched at the estuary mouth and in upper Burns Bay. Cadmium and Ni concentrations were not significantly enriched.

Chrome, Cu, Pb and Zn concentrations in the surficial sediments of Lane Cove estuary increased from 1999 to 2010 by approximately 90%, 75%, 50% and 50%, respectively, in upper Burns Bay, whilst Cu, Pb and Zn concentrations increased at the mouth of the estuary by about 60%, 50% and 15%, respectively (Fig. 6e).

In Burns Bay (LC-C4), Cr concentrations were significantly higher than for other metals, however concentrations have recently declined substantially, similar to Pb, whereas Cu concentrations have increased to the present and Zn has remained constant (Fig. 5e to h). Background for all metals was at 50 cm sediment depth at this location, except for Cr (>60 cm). In Woodford (core LC-C1), Alexandra (core LC-C2) and Tambourine Bays (core LC-C3), Cr, Cu, Pb and Zn concentrations were stable at the top of cores and background was at 18 cm, 100 cm and 70 cm sediment depth, respectively. At the mouth of Lane Cove estuary (core LC-C5), Cu and Pb concentrations increased to the top of the core, whereas Cr and Zn remained constant.

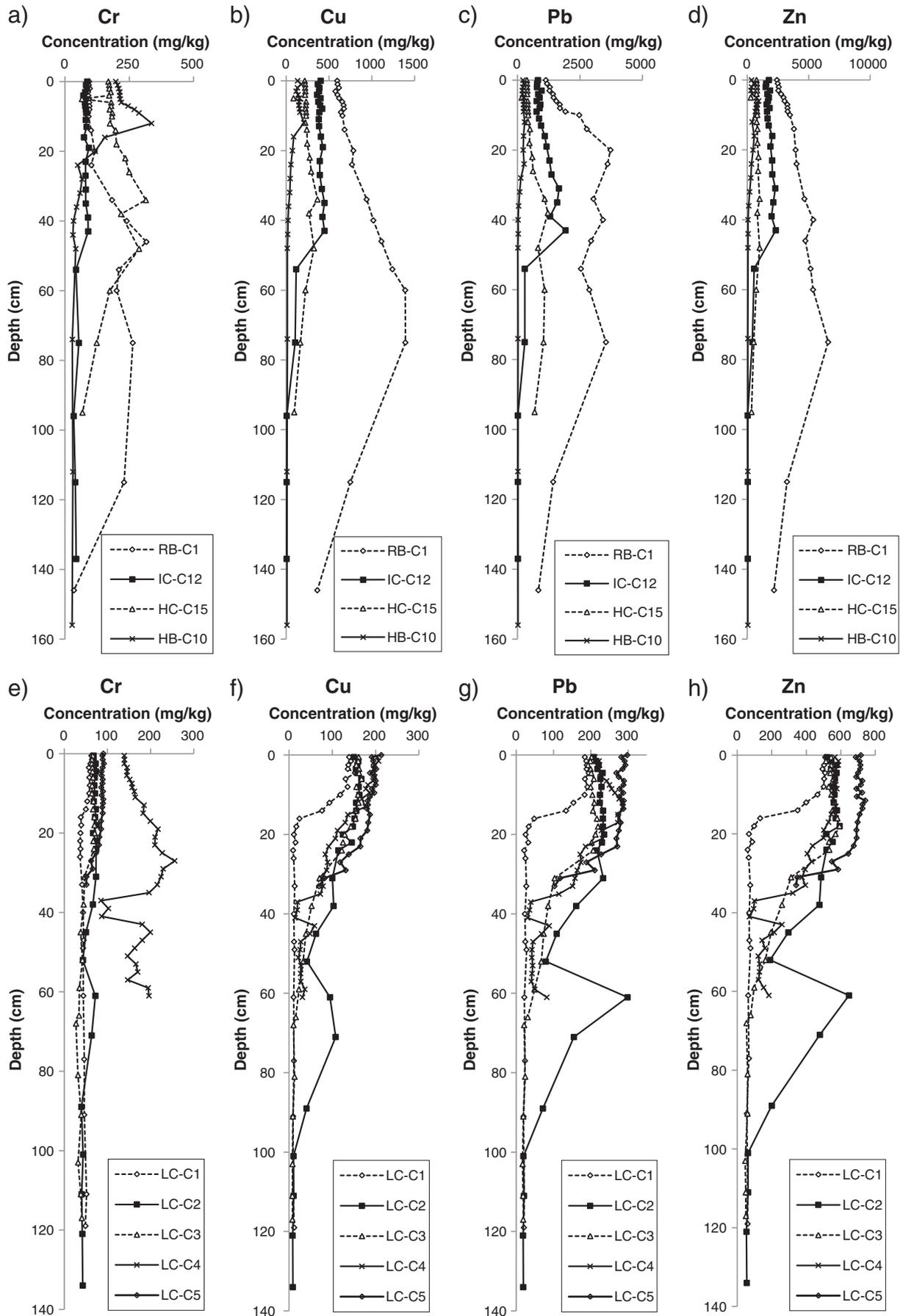


Fig. 5. Subsurface (core) sediment metal concentrations. (a) Cr, (b) Cu, (c) Pb, (d) Zn in Blackwattle/Rozelle Bay, Iron Cove, Hen and Chicken Bay and Homebush Bay, respectively; (e) Cr, (f) Cu, (g) Pb, (h) Zn in Lane Cove; and (i) Cr, (j) Cu, (k) Pb, (l) Zn in Middle Harbour.

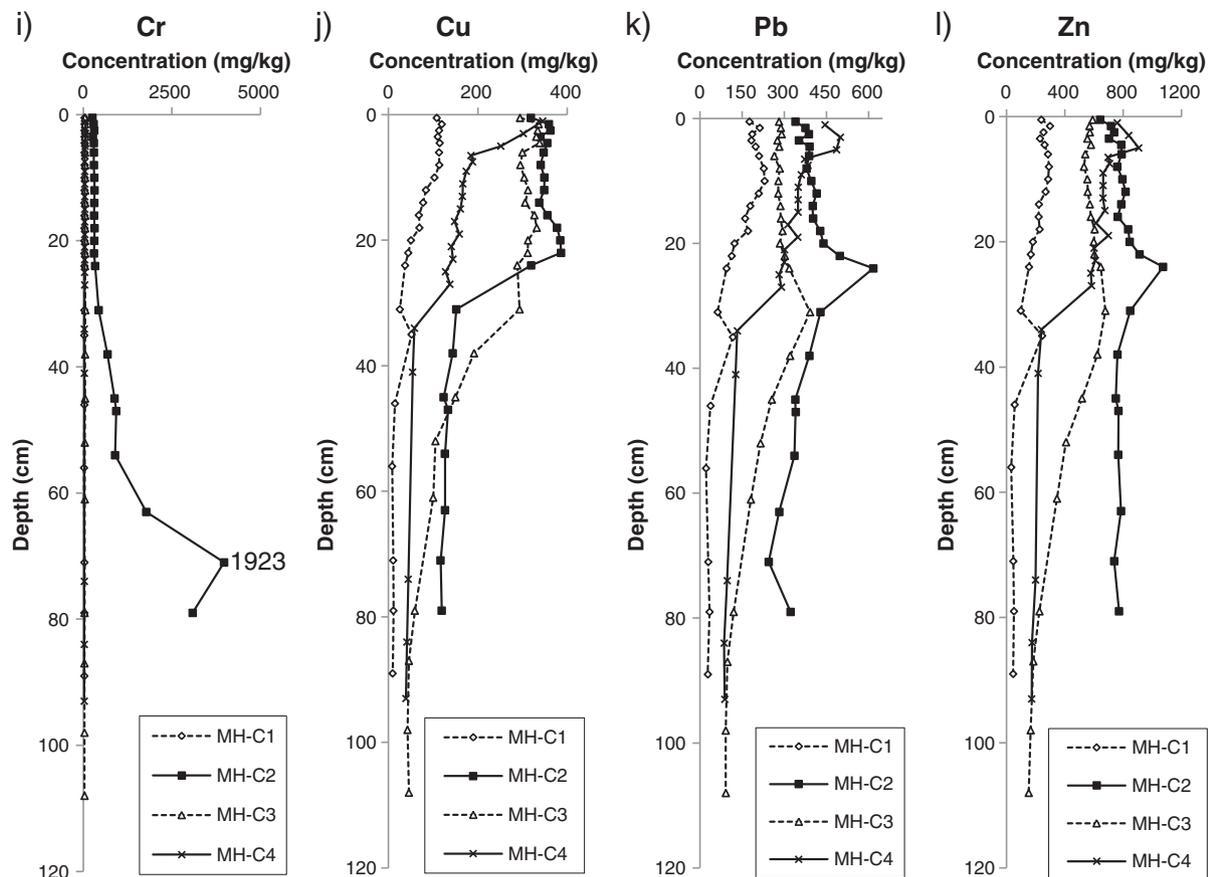


Fig. 5 (continued).

3.6. Middle Harbour

In the 2010 survey sediment in the upper reaches of embayments adjacent to major fluvial inputs was sandy (50–85% sand), as well as at the mouth of the estuary. The central, deep basin was mantled in mud (>90% mud), except for a few isolated areas where mud content was relatively low (57–71%). The distribution of Cu, Pb and Zn was similar, i.e., low concentrations in the upper harbour, the main basin and the harbour mouth, with highest levels in Sugarloaf and Long Bays and moderate concentrations in Sailors Bay (Fig. 4g & h). Nickel concentrations were near background and Co concentrations were generally low with minor enrichment in Sugarloaf and Long Bays. Chromium was significantly elevated in Sugarloaf Bay sediments.

Copper concentrations have increased in Sailors Bay between 1996 and 2010 and declined in Sugarloaf, and possibly Quakers, Bays (Fig. 6d), trends that are supported by core data (MH-C2 and MH-C3). Copper concentrations in the deep mud basin have increased marginally over the last 14 years. Lead concentrations have declined in the upper reaches of all embayments of Middle Harbour, especially Long Bay and increased marginally in sediments of the mud basin over this period. Zinc concentrations were higher in 1996 than in 2010 in Long, Sailors and Sugarloaf Bays, as well as in upper Middle Harbour and have possibly decreased in Quakers Bay.

Concentrations of Cr, Cu, Pb and Zn decreased in the top 10 cm of sediment in upper Middle Harbour (Core MH-C1) and background was at 55 cm sediment depth (Fig. 5i–l). In Sugarloaf Bay, Zn and Pb declined in the top 30 cm of sediment (Core MH-C2), however Cr and Cu remained constant over this interval. Core MH-C2 failed to penetrate pre-anthropogenic sediment (total depth of core 80 cm). Copper and Zn increased in the upper 10–20 cm of sediment in Sailors Bay (Core MH-C3), whilst Cr and Pb remained stable over

this period. In Long Bay, Pb and Zn increased in the upper 30–15 cm sediment depth (Core MH-C4) before declining to the surface, whereas Cu increased significantly from 15 cm sediment depth to the top of the core.

4. Discussion

Comparison of sedimentary metal concentrations, on both temporal and spatial bases, needs to be undertaken on a normalised basis to reduce confounding by variable grain size (Loring, 1991; Birch, 2003; Mudge et al., 2003; Birch et al., 2008a, 2008b). Sediments covering Sydney estuary contain some of the highest concentrations of metals reported globally (Table 2) and in Australia (Table 3). Of the six embayments studied, sedimentary metal concentrations are highest in Rozelle and Blackwattle Bays, followed closely by Iron Cove, for both total and size-normalised sediments (Table 4).

Background concentrations obtained in the present study were similar to published values for Sydney estuary (Table 5), however background varied across the estuary, especially for Cr (29–51 mg/kg) and Pb (17–33 mg/kg). Weathering of the Wianamatta Group shales and Hawkesbury sandstones comprising bedrock of Sydney estuary catchment has produced numerous primary soil landscapes (Herbert, 1983), which may have resulted in slightly different background concentrations across the catchment. In the current study, specific background values were used for individual embayments to obtain the most accurate determination of enrichment factors.

4.1. Metal enrichment

Enrichment factors (EFs) provide a measure of how far the environment has moved away from the pristine condition (Birch, 2012).

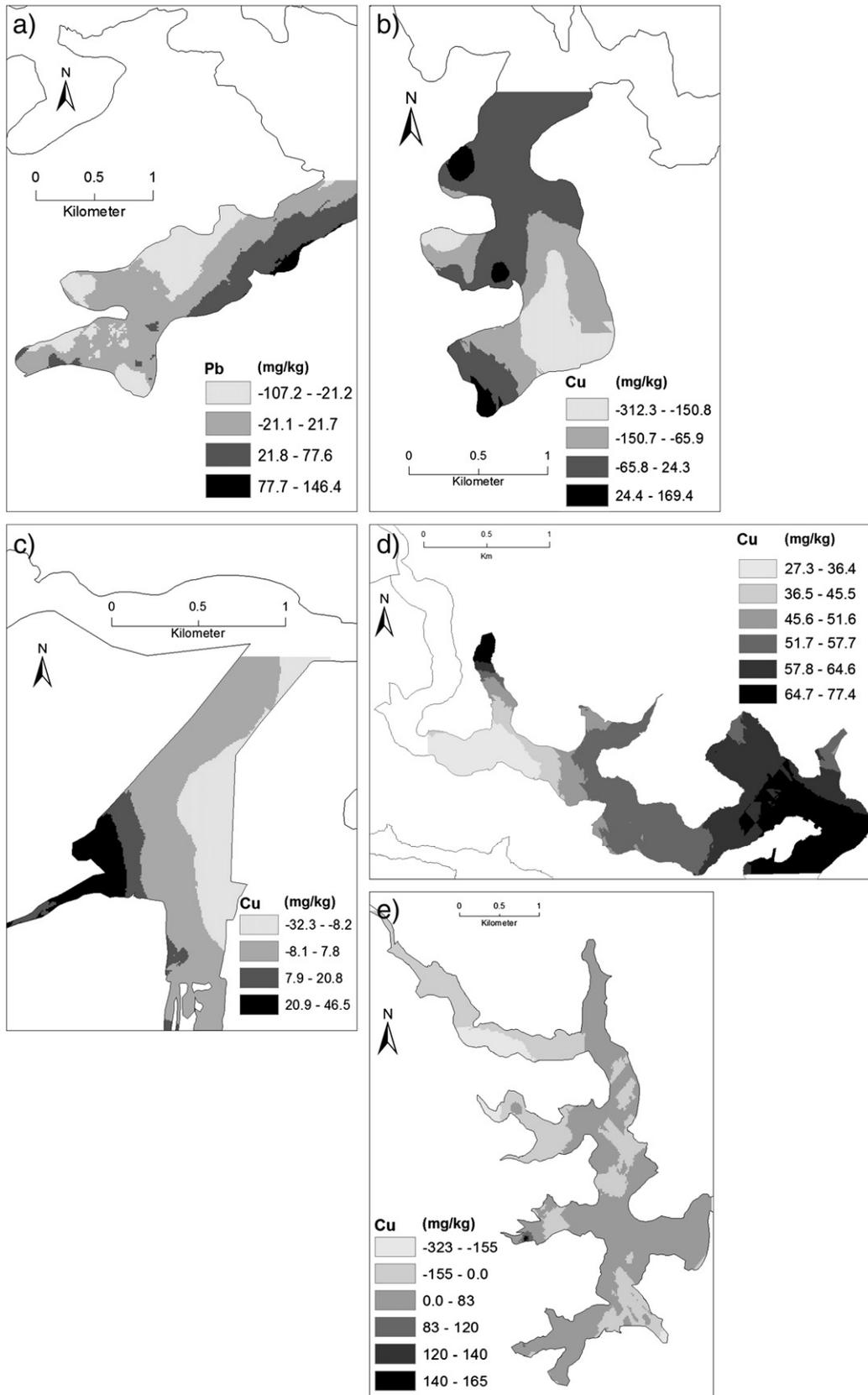


Fig. 6. Change in metal concentrations between vintages of surficial sediment surveys. (a) Pb in Iron Cove 2000 to 2009, (b) Cu in Hen and Chicken Bay 2004 to 2010, (c) Cu in Homebush Bay 2004 and 2010; (d) Cu in Lane Cove 1996 and 2010 and (e) Cu in Middle Harbour 1999 and 2010.

Mean EFs are highest for Rozelle and Blackwattle Bays (EFs = 39, 28 and 32 for Cu, Pb and Zn in 2010, respectively) and the majority decline with distance from the central business district (CBD) to 12, 11 and 15,

respectively, in Homebush Bay and 16, 11 and 9, respectively, in Lane Cove estuary (Table 6). EFs for Co and Ni in 2010 were <3 in all areas, indicating “minor” anthropogenic influence and were below 1.5 times

Table 2
Sydney estuary and global normalised (<62.5 µm) metal concentrations (mg/kg) in surficial sediment.

Estuary		Cd	Co	Cr	Cu	Ni	Pb	Zn
Sydney estuary, Australia ^a	Mean	0.8	8.3	na	188	21.7	364	651
	Range	bd–24.3	2.2–54	na	9.3–1053	5.0–245	37.9–3604	108–7622
Hong Kong, China ^b	Mean	0.33		49	119	25	54	148
	Range	0.1–5.3		5–560	1–4000	5–220	9–260	17–790
Quanzhou Bay Quanzhou, China ^c	Mean	0.59		82	71	33	68	180
	Range	0.3–0.9		51–122	25–120	16–46	34–101	106–242
Tamaki Estuary Auckland, New Zealand ^d	Mean	0.28			35		73	207
	Range	0.1–1.0			21–47		51–122	138–272
Qua Iboe Estuary Niger Delta, Nigeria ^e	Mean			0.014	44	21	45	102
	Range			0.01–0.02	43–45	21–21	43–46	102–104
Lima Estuary Viana do Castelo, Portugal ^f	Mean			57	45	14	37	111
	Range			24–84	16–406	46,447	19–64	59–398
Port of Barcelona Barcelona, Spain ^g	Mean	1.22		68	183	25	189	391
	Range	0.4–2.8		39–110	71–531	18–34	86–589	183–1133
Gulf of Gemlik Sea of Marmara, Turkey ^h	Mean		19	117	41	110	29	128
	Range		13–24	71–181	23–58	35–165	0.1–67	88–185
San Pablo Bay San Francisco, U.S.A. ⁱ	Mean	0.21		21	39	37	22	65
	Range	0.1–0.4		15–39	25–49	27–45	15–27	48–79
Montevideo Harbour Montevideo, Uruguay ^j	Mean			161	89	30	85	312
	Range			79–253	59–135	26–34	44–128	174–491
Gulf of Paria Venezuela/Trinidad ^k	Mean			29	14	18	13	89
	Range			10–40	5–22	5–24	1–37	48–158

na—not available.

^a Birch and Taylor (1999).

^b Zhou et al. (2007).

^c Yu et al. (2008).

^d Abraham and Parker (2008).

^e Udofia et al. (2009).

^f Cardoso et al. (2008).

^g Guevara-Riba et al. (2004).

^h Ünlü et al. (2008).

ⁱ Lu et al. (2005).

^j Muniz et al. (2004).

^k Rojas de Astudillo et al. (2005).

background in Lane Cove (no enrichment) (Table 6). The EF in 2010 exceeded 10 times, i.e., “very severe” anthropogenic modification, for Cu, Pb and Zn in all six embayments investigated, except Zn in Lane Cove estuary (EF 9).

The National Land and Water Resources Audit of the 970 estuaries in Australia, based mainly on catchment land use and estuarine attributes, classified Sydney estuary as “extensively modified” (OzCoast, 2000). This rating is supported by our classification of “very severe modification” based on EFs > 10 for Cu, Pb and Zn for the majority of the areas investigated in the current study.

4.2. Mean enrichment quotients

Mean enrichment quotients (MEQs) provide an ‘average’ enrichment of three metals (Cu, Pb and Zn) for temporal and spatial comparisons (Table 6). The MEQ for the entire Sydney estuary for the three metals is 12.6 (Birch and Olmos, 2008), indicating that Rozelle and Blackwattle Bays (MEQ = 39), Iron Cove (MEQ = 26) and Hen and Chicken Bay (MEQ = 21) are substantially more impacted than the majority of the waterway. High MEQs are strongly correlated to catchment landuse (Birch and Olmos, 2008) and these three embayments are the most highly urbanised catchments of Sydney estuary.

4.3. Temporal trends

Earlier attempts (Taylor, 2000; Birch and Taylor, 2004) at using vintage sets of surficial sediment metal distributions to detect changes in contamination of estuary beds, showed generally decreasing Cu, Pb and Zn concentrations in sediment mantling upper Sydney estuary and increasing concentrations in the lower waterway. The latter studies used sparse data from a 1977 survey (Irvine, 1980) and a dense data set from the late 1990s and the different sampling densities between the two studies resulted in poor resolution. A more

Table 3

Sydney estuary and Australian normalised (<62.5 µm) metal concentrations (mg/kg) in surficial sediment.

Estuary		Cu	Pb	Zn
Sydney estuary ^a (six embayments)	Mean	217	332	721
	Range	137–432	220–694	538–1569
Burrill Lake ^b	Mean	76	33	100
	Range	41–119	18–55	57–299
Durras Lake ^b	Mean	29	24	123
	Range	21–46	20–28	94–144
Myall Lakes ^b	Mean	5	19	49
	Range	2–9	5–28	12–82
St Georges Basin ^b	Mean	75	28	100
	Range	10–318	17–55	54–256
Pittwater ^b	Mean	87	65	134
	Range	25–596	20–174	20–272
Brisbane Water ^b	Mean	30	57	157
	Range	13–153	26–362	76–775
Port Jackson ^b	Mean	181	274	578
	Range	31–727	49–1302	86–1925
Georges River/ Botany Bay ^c	Mean	70	155	393
	Range	17–457	29–924	76–2641
Hawkesbury River ^d	Mean	47	55	135
	Range	17–203	19–174	68–272
Hunter River ^e	Mean		172	
	Range	35–193	48–777	31–1638
Port Philip Bay ^f	Mean	13	30	202
	Range	1–62	1–197	13–1600

^a Present work.

^b Birch and Olmos (2008).

^c Birch et al. (1996).

^d Birch et al. (1998).

^e Birch et al. (1997, 1998).

^f Fabris et al. (1999).

Table 4
Minimum, mean and maximum metal concentrations (mg/kg) in Sydney estuary sediments.

Location		Cd	Co	Cr	Cu	Ni	Pb	Zn
<i>Total sediment</i>								
Rozelle Bay & Blackwattle Bay (n = 30)	Mean	na ^a	6.8	66	330	23	554	1178
	Range	na	1.1–9.2	37–105	42–574	4–49	84–1114	125–2824
Iron Cove (n = 30)	Mean	na	8	77	204	19	372	827
	Range	na	3.5–10	40–109	92–332	10–26	216–783	390–1955
Hen and Chicken Bay (n = 38)	Mean	na	10.7	169	353	20	313	759
	Range	na	6.0–13.8	33–216	42–647	4–24	80–499	151–1259
Homebush Bay (n = 31)	Mean	na	11.6	164	127	30	254	622
	Range	na	8.6–14.4	54–265	67–143	17–85	118–604	253–984
Lane Cove estuary (n = 32)	Mean	0.6	6.1	56	129	15	177	428
	Range	0.05–1.4	0.7–10	4–132	6–202	1–22	17–288	26–671
Central Middle Harbour (n = 28)	Mean	0.7	3.2	49	124	9.9	177	374
	Range	0.07–2.1	0.2–6.9	2.6–190	4–424	0.9–22	10–817	1096
<i>Fine (<62.5 µm) sediment</i>								
Rozelle Bay & Blackwattle Bay (n = 30)	Mean	na	7.8	79	432	28	694	1569
	Range	na	6–10	63–125	218–757	18–56	362–1482	758–3392
Iron Cove (n = 30)	Mean	na	9.5	100	269	23	501	1047
	Range	na	7.2–11.8	75–127	184–384	19–28	362–872	735–1846
Hen and Chicken Bay (n = 38)	Mean	na	10	148	317	21	277	735
	Range	na	5.3–12.6	66–218	84–636	9–25	147–405	299–1106
Homebush Bay (n = 31)	Mean	na	13.5	182	138	32	271	743
	Range	na	10–33	81–251	87–173	23–70	115–647	343–2871
Lane Cove estuary (n = 32)	Mean	0.7	8	71	161	20	220	538
	Range	0.6–1.3	5–10	52–135	125–198	15–22	148–288	382–671
Central Middle Harbour (n = 42)	Mean	0.9	6	88	220	18	274	579
	Range	0.5–2.4	4–11	34–287	123–516	4–28	128–868	340–1511

^a na—not available.

detailed examination of sediments in Hen and Chicken Bay (Butland, 2004), using multiple time series data, provided a more detailed indication of decreasing surficial sediment Cu, Pb and Zn concentrations in the embayment. High-density sampling and the use of specially-located, dated cores provided a detailed view of historic changes in bottom sediment contamination in other, nearby, estuaries and an estimation of future spatial trends in pollution of surficial material in these waterways (Olmos and Birch, 2010; Birch et al., 2012).

Success in determining changes in surficial sediment metal contamination is dependent on the sedimentation rate, the nature and rate of change in supply, the frequency of surveys and sampling density. The advantage of using surficial sediments to determine temporal change is the wide spatial coverage achieved, whilst cores provide a continuous record of temporal change for one location only. The probability of error in determining the magnitude of change in surficial sediment concentrations obtained from vintage data will increase with distance from core locations. However, a combination of these two techniques provides a powerful tool to obtain a comprehensive understanding of historical change in contaminant supply and dispersion.

The majority (55) of the 60 cores taken throughout Sydney estuary in the 1970s (Irvine, 1980; Irvine and Birch, 1998) showed an increase in metal concentrations towards the sediment surface and many (8) cores displayed steeply increasing trends at the top of the cores (Fig. 7). These patterns indicated that metal concentrations were still increasing throughout most of the estuary at this time and very rapidly in some localities (Fig. 8). Metal concentrations continued to increase for 3 (of 12) dated cores (²¹⁰Pb, ¹³⁷Cs) taken in the mid 1990s, located mainly in the tributaries of Lane Cove and Middle Harbour, whilst three cores in Iron Cove had consistent concentrations towards the top (Taylor, 2000; Taylor et al., 2004).

Temporal trends were investigated in the present study using GIS-mapped distributions of several vintages of surficial sediment metal data and sedimentary cores, specifically located to test results from the surficial sediment analysis and to identify changes in contaminant supply at major input points. An examination of mean surficial sediment metal concentrations for various vintages of data (Table 7) showed that levels in Blackwattle and Rozelle Bays and Iron Cove have increased, whereas metal concentrations in the other four embayments

Table 5
Pre-anthropogenic metal concentrations (mg/kg) for Sydney estuary.

Location	Cd	Co	Cr	Cu	Ni	Pb	Zn
Central embayments (n = 5) ^a	na ^a	6	35	10	13	17	47
Central embayments (n = 5) ^b	na	na	na	9	na	17	46
Lane Cove Estuary (n = 16) ^c	0.7	7	42	10	16	21	59
Central Middle Harbour (n = 5) ^d	0.6	3	29	11	12	30	47
Sydney estuary (n = 60) ^e	na	16	51	10	26	33	47
Sydney estuary (n = 4) ^f	na	na	na	12	na	20	48
Sydney estuary (n = 12) ^g	na	na	na	12	na	23	53
Range across estuary/studies	0.6–0.7	3–16	29–51	9–12	12–16	17–33	46–59

na—available.

^a Present work.^b Chang (2010).^c Lee (2010).^d Churchill (2011).^e Irvine and Birch (1998).^f Birch and Taylor (1999).^g Birch and Olmos (2008).

Table 6
Metal enrichment in current and vintage surficial sediment data sets.

Embayment		Survey date	n	Co	Cr	Cu	Ni	Pb	Zn	MEQ
Rozelle Bay & Blackwattle Bay	Mean	2004	10	1.3	2.3	34	2	34	23	30
	Mean	2010	34	1.3	2.3	43	2.2	41	33	39
	Maximum	2010	34	1.8	3.6	76	5.5	101	72	83
Iron Cove	Mean	1975	10	3.8	2.6	18	3.3	22	17	19
	Mean	2000	45	1.6	2.6	24	1.8	30	23	26
	Mean	2009	30	1.6	2.9	27	1.8	29	22	26
	Maximum	2009	30	2	3.6	38	2.2	51	39	43
Hen and Chicken Bay	Mean	1975	10	3.8	5.3	42	3	20	15	26
	Mean	2001	31	1.6	4.9	43	1.6	22	18	28
	Mean	2004	42	1.9	4.8	32	1.7	19	15	22
	Mean	2010	39	1.7	4.2	32	1.5	16	16	21
	Maximum	2010	39	2.1	6.2	64	1.9	24	21	36
Homebush Bay	Mean	1975	10	4.6	9	15	3.9	15	19	16
	Mean	2004	22	2.2	5.3	14	2.6	16	14	15
	Mean	2010	34	2.3	5.2	14	2.4	16	16	15
	Maximum	2010	34	5.4	7.2	17	5.4	38	33	29
Lane Cove Estuary	Mean	1999	67	1	1.4	10	1	8	7	9
	Mean	2010	32	1.1	1.7	16	1.2	11	9	12
	Maximum	2010	32	1.5	3.2	20	1.4	14	11	na
Middle Harbour	Mean	1996	107	2	na	21	1.8	13	13	16
	Mean	2010	42	2	3	20	1.5	9	12	11
	Maximum	2010	42	3.6	10	47	2.3	29	32	23

na—not available.

have mostly decreased. These results are in contrast to temporal distributions obtained from GIS-mapped surficial sediment and core data, which showed consistent decreases throughout the six embayments. This inconsistency is due to differences in sample distributions and densities in multiple data sets and highlights the risk of using statistical data alone in judging temporal change in environmental indicators.

4.3.1. Blackwattle/Rozelle Bays

Insufficient spatial sampling density in previous studies of these bays precluded determination of temporal trends in metal distributions from surficial sediment data. Extraordinarily high Cu, Pb and Zn concentrations in Blackwattle (950 mg/kg, 2500 mg/kg and 4000 mg/kg, respectively) and Rozelle Bays (1200 mg/kg, 3200 mg/kg and 6800 mg/kg, respectively) indicated intense industrial activity in adjacent catchments. Maximum concentrations were at sediment depths of 20 cm and 80 cm, respectively, which equate to dates of 1956 and 1963, respectively (Taylor, 2000; Taylor et al., 2004). Similarly high concentrations of Ni (60 mg/kg and 120 mg/kg, respectively) and Cr (250 mg/kg and 590 mg/kg, respectively) in these two embayments were additional evidence of such activity. The onset of contamination was interpreted as approximately 1866 and 1930 for these embayments, respectively (Taylor et al., 2004). The vertical distribution of these metals suggested that industrial activity continued for a considerable period in Blackwattle Bay (90 years) but was shorter (30 years) and more intense in Rozelle Bay, a hypothesis supported by historical records for the catchment (Links, 1998; Nikandrow, 2000; Taylor et al., 2004). The concentration of all metals has been declining for a longer period in Blackwattle Bay (about 54 years) than Rozelle Bay (approximately 46 years) and concentrations of Co, Cr, Cu, Ni, Pb and Zn are currently similar in both bays, indicating that relaxation rates have been greater in Blackwattle Bay over this period. Intense industrial activity took place on the majority of the foreshore of these two bays (Nikandrow, 2000), supplying metals to most of the bay area. However, present-day maximum surficial metal distributions were confined to adjacent Whites and Johnsons Creeks, indicating that stormwater has superseded industrial supply as the major source of metals to these embayments in recent times.

4.3.2. Iron Cove

Surficial sediment distribution of Cu, Pb and Zn in Iron Cove in 1975 and 2000 exhibited similar spatial patterns, i.e., an increase in

concentrations near the two inlets to the Cove, suggesting that stormwater runoff remained the predominant source during this period. Chrome concentrations in surficial sediments increased greatly at the mouth of the cove between 1975 and 2000, suggesting a continuous source of this metal from the main estuary channel during this period.

The concentrations of metals in surficial sediment in the majority of Iron Cove declined between 2000 and 2009. However, Cu, Pb and Zn increased adjacent to the mouths of the two creeks entering the embayment. These increasing metal concentrations obtained from surficial sediment data sets were in contrast with evidence provided by cores taken at the mouths of these creeks. Increasing concentrations in surficial metal data were due to short-term reversals (<9 years) in an otherwise long-term (30–49 years) declining trend observed in the cores. The successful interpretation of surficial sediment data in the current study was greatly assisted by constraints provided by the core results, as exemplified in this case.

4.3.3. Hen and Chicken Bay

A general decline in surficial metal concentrations in Hen and Chicken Bay between 1975 and 2001, together with a continued improvement between 2004 and 2010, suggests a significant reduction in supply from the catchment over this period. An exception is an increased Zn in sediments mantling Canada Bay in the south. However, the elevated Zn concentration determined from surficial sediment data remained unconfirmed by core evidence due to an erratic Zn trend in the top 20 cm of the core. Moreover, detailed work (Butland, 2004) on multiple vintages of data over the period 1977–2004 demonstrated strong declining surficial sediment Cu, Pb and Zn concentrations across all of Hen and Chicken Bay. A reduction in sedimentary metals may be associated with the removal of industry from the catchment, especially from the foreshores of the embayment, a process for which evidence is available.

A maximum Pb concentration (1200 mg/kg) at 45 cm sediment depth in core HC C15, adjacent to the northwest shoreline of Hen and Chicken Bay, is related to the location of a white lead factory (British-Australia Lead Manufacturers Pty. Ltd., BALM), which commenced operations in 1921 (Townsend, 2011) (Fig. 2b, #1). Dulux Paints bought BALM in 1960 and continued to manufacture lead-based paints until the plant closed in 1995 (Townsend, 2011). Today the site is a medium-density housing estate (Townsend, 2011). The large decline in Pb concentration (1200 mg/kg to 400 mg/kg) in this core is testament to the benefits of removing shore-based industry.

The source of high Cu concentrations (mean 317 mg/kg and maximum 636 mg/kg), which characterise surficial sediments covering Hen and Chicken Bay, is related to a copper cast foundry (G. E. Crane, later becoming Australia Bronze Crane Copper Ltd.—Austral Bronze) located on reclaimed land directly adjacent to the highest sediment Cu concentrations in Canada Bay (Fig. 2b, #2).

4.3.4. Homebush Bay

Copper, Pb and Zn decreased in surficial sediments between 1977 and 2004, except in the southeast adjacent to Powells Creek, whilst Co, Cr and Ni declined in surficial sediments throughout the bay. These trends were supported by data from two cores in the current study (HC-C10, C11), as well as a core (HB-3) obtained by Taylor et al. (2004).

Increased Cu concentrations at the mouth of Haslams Creek between 2004 and 2010 is not verified by coring. However, increased Ni and Zn concentrations in sediment adjacent to Powells Creek is supported by core data and reflects increased supply from the adjacent catchment.

The slightly increased Co, Ni and Zn in sediments adjacent to the mid-eastern shore of Homebush Bay, between 2004 and 2010, is possibly due to runoff related to extensive remediation of contaminated

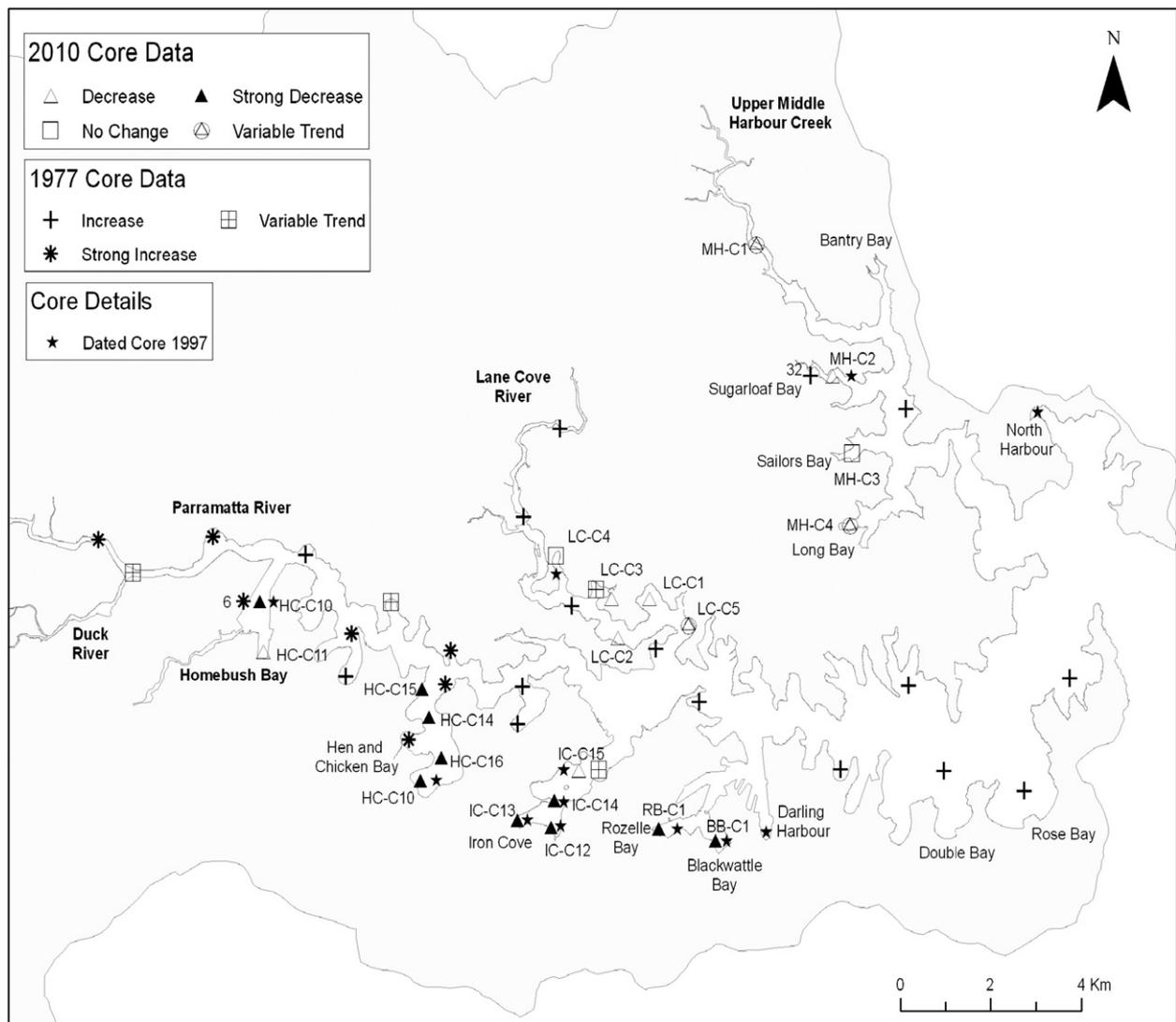


Fig. 7. Sediment core locations and temporal trends for vintages of surveys (1977, 2004, 2010).

soils on the adjacent Rhodes Peninsula (Auburn City Council, 2005; Thiess Services, 2010; NSW Maritime, 2010) (Fig. 2c, #3).

High Pb concentrations in sediment opposite the south-eastern shoreline in Homebush Bay is located adjacent to a site where paint factories operated for almost 70 years (Fig. 2c, #4). Berger Paints began operations in 1919, including storage of lead carbonate. The factory changed hands many times and considerable quantities of Pb by-products had leached into the bay by the time it closed in 1988 (Legislative Council, 2002). Soil and sediment (3600 m², or 2900 t) were declared a risk to human health due to elevated Pb levels (up to 90,000 mg/kg) (NSW O E and H, 2011). Pb-contaminated materials (including mangroves) were excavated to a depth of 1 m and removed in 2006/7, and replaced with clean soil, and sediment and new mangroves at a cost of \$0.6 million. High Pb concentrations observed in the present investigation in sediment adjacent to this area, together with evidence of increased Pb concentrations between 2004 and 2010, indicated a continued Pb supply to the bay in this area, possibly via surface or subsurface waters from the adjacent catchment.

Extensive remedial dredging of estuarine sediment was undertaken in Homebush Bay to reduce risks associated with high concentrations of organic contaminants, mainly dioxins (Fig. 2c, #3). The top 0.5 m of sediment of an area 50 m wide and 1400 m long, adjacent to the eastern shoreline of Homebush Bay, was removed and in-filled with clean gravel (Thiess Services, 2009). Dredging of the area (8.5 ha, or

42,500 m³, or ~70,000 t) was completed in 2010 at a cost of \$21 million. The texture of surficial sediment in this area changed from mud in 2004 to mainly gravel in the present study. However, although less than a year has elapsed since completion of the remedial effort, mud has been re-suspended, transported and deposited on top of the gravel to a thickness of approximately 4 cm in the south. This process has resulted in a decline in Cr, Cu and Pb surficial concentrations in the remediated zone, however the magnitude of decrease is not considerable (<50 mg/kg) considering the short interval between field sampling in the present study and remediation (6 months).

4.3.5. Lane Cove

Minor increases in concentrations of Cu, Pb and possibly Zn in sediments at the mouth of Lane Cove between 1999 and 2010 are due to influx of metal-rich particulate matter from the central channel of Sydney estuary. Concentrations of Co, Pb and Zn in Lane Cove are highest in this location, which is testament to the importance of this source. Increased concentrations of Cr, Cu and Zn in surficial sediment in Burns Bay were verified by core data. Chrome is a major ingredient in the process of tanning animal hide and the high concentrations (140 mg/kg) of this metal are related to a large tannery (Pioneer Tannery), which operated between the 1880s and 1941 (Fig. 2f). Maximum Cr concentrations were at 30 cm sediment depth, which relates to approximately 1950 (Taylor et al., 2004), however concentrations

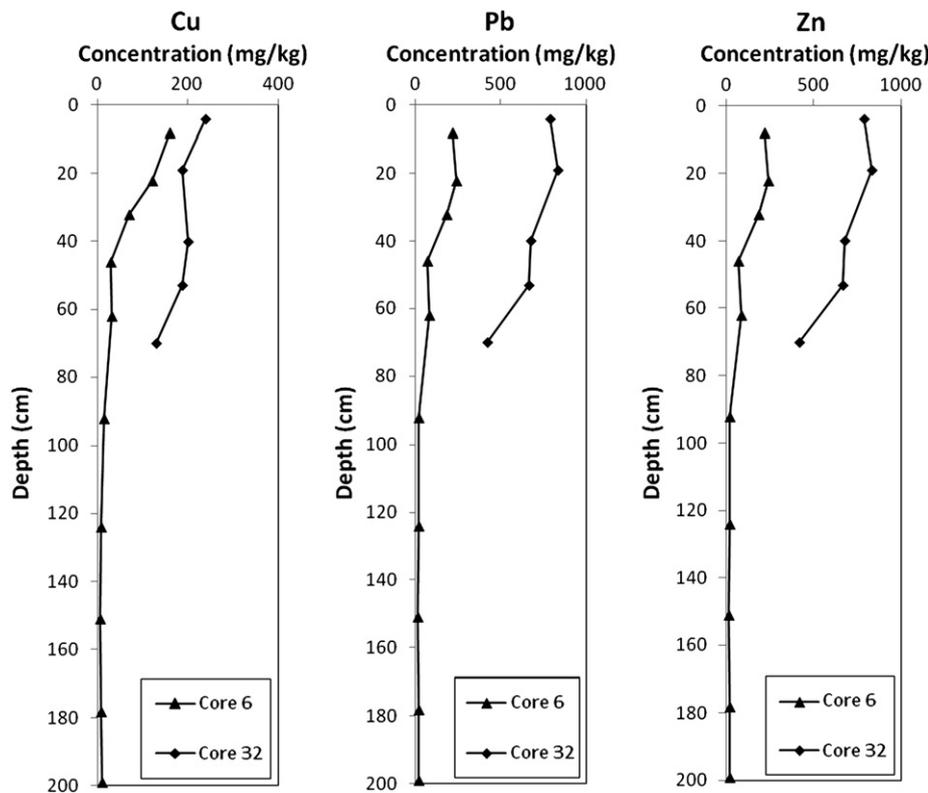


Fig. 8. Increasing metal concentrations at the top of cores taken in 1977.

remain high (>200 mg/kg) to the bottom of the core (60 cm) (~1900, Taylor et al., 2004). Although Cr concentrations have declined rapidly in recent times, Cr levels in surficial sediment in Burns Bay were considerably higher than elsewhere in Lane Cove, possibly related to the three tanning pits that remain intact at the site, or to remobilisation of Cr rich fluvial soils and sediments. No significant supply of metals was observed from Lane Cove River itself, which is a large potential point source. A reason for the lack of supply is not obvious, but is supported by a previous extensive investigation of the cove (LCEC, 1999).

4.3.6. Middle Harbour

The maximum Cr concentration (4000 mg/kg at a sediment depth of 70 cm) in the core retrieved from Sugarloaf Bay (MH-C2) was dated at 1923 by Taylor et al. (2004). Tanneries were first established in the adjacent Scotts Creek catchment in 1869 (James Forsyth Rosewall Tannery, renamed Enterprise Tannery in 1906) and were soon scattered throughout the valley, using the plentiful supply of wattle trees and water, until the last tannery closed in 1992 (Birmingham et al., 1979; Willoughby Council, 2010) (Fig. 2d, #5). Chrome concentrations declined rapidly up the core, however at 50 cm sediment depth, equivalent to 1935 (Taylor et al., 2004), they are still at 1000 mg/kg. Concentrations decrease slowly above this point and currently remain high (250 mg/kg) at the sediment surface, compared to regional levels (35–65 mg/kg). The vertical distribution of Cr in the core suggests that either the industry did not remain at high production levels for long (12 years), persisting for many years thereafter at lower activity levels, or that reworking of contaminated soils and fluvial sediments in Scotts Creek valley maintained supply of Cr to the embayment. Scotts Creek drains the East Chatswood industrial/commercial area, which has developed extensively in the last 30 years (Taylor et al., 2004). However, the core taken in the present study shows a steady decline in Cu, Pb and Zn concentrations towards the sediment surface, suggesting a decreasing supply from this complex in recent times.

The strong increase in Cr, Cu, Pb and Zn concentrations towards the top of the core MH-C4 obtained from Long Bay, is a reflection of the poor water quality discharged by Flat Rock Creek at the head of the embayment (NSW Public Works, 1994; Sydney Water, 1998; MPR, 2005) (Fig. 2d, #6). Flat Rock Creek (Gully), originally a natural valley with waterfalls and a tidal estuary, has been severely modified by both an incinerator and an industrial and domestic landfill 30 m thick (Willoughby City Council, 1995), with groundwater leachate from the tip possibly contaminating the creek (Woodward Clyde, 1993). Dredging of sediments in 1997/8 in upper Long Bay and construction of a detention basin at the mouth of Flat Rock Creek may explain the recent, short-term declining metal trend in the upmost few centimetres of surficial sediment in this core.

4.4. Recent declining surficial metal trend

The general declining trend in metal concentrations in surficial sediment mantling the four southern embayments (Blackwattle/Rozelle Bay, Iron Cove, Hen and Chicken Bay and Homebush Bay) is due, in part, to a slow movement of industry out of these catchments (Collett, 1979; Russell, 1982; Taylor et al., 2004). In addition, legislation, e.g. the State Pollution Control Commission Act 1970, the Clean Waters Act 1978, the Coastal Protection Act 1979 and the Catchment Management Act 1989, which prohibited the dumping of waste, reformed pollution licensing and enforced control procedures (Smith, 1997) have probably assisted in the declining surficial sediment metal concentrations and improved estuarine condition.

The decrease of Pb in sediment from all parts of the current study area has been attributed to the progressive phasing out of leaded petrol since 1985, when all petrol-engine cars sold in Australia had to use unleaded petrol (Taylor et al., 2004). Declining petrol Pb usage is strongly correlated with a decrease in atmospheric Pb (O'Connor, 1990; Lawrence, 2005) and declining Pb concentrations

in surficial sediment in local waterways (Birch and McCready, 2009; Birch, 2011).

4.5. Relaxation rates and predicted interval to reach acceptable surficial sediment concentrations

Surficial sediment concentrations of Cu, Pb and Zn modelled for 2020 and the time required to reach twice background concentrations (the concentration taken to be an acceptable level in the current study) are provided in Table 8. Whilst no temporal information was available from vintage surficial sediment data in Rozelle/Blackwattle Bays, cores taken in the area showed strong declining trends towards the top of the cores for Cu, Pb and Zn. Trendlines for the core taken in Blackwattle Bay showed that Cu and Zn concentrations remain high (383 mg/kg and 927 mg/kg, respectively) in 2020. These metals will take 60 and 20 years, respectively, to reach two times background level, whereas for Pb it would only take 10 years. In Rozelle Bay, Cu and Zn concentrations were calculated to decrease to similar levels as Blackwattle Bay (319 mg/kg and 1271 mg/kg, respectively) by 2020, but would take less time (23 years and 19 years, respectively) to reach two times background due to a higher sedimentation rate. Lead concentrations were predicted to decline to background by 2020.

Trendline concentrations modelled for surficial sediment in 2020 adjacent to Hawthorne Canal in Iron Cove remained high (116 mg/kg, 291 mg/kg and 1086 mg/kg for Cu, Pb and Zn, respectively) by 2020 and would take 15, 19 and 42 years, respectively, at present input rates (Table 8) to decline to two times background. In central Iron Cove, predicted concentrations decreased to 123 mg/kg, 272 mg/kg and 477 mg/kg for Cu, Pb and Zn, respectively, by 2020 and it would take approximately 20 years for these metals to reach two times background. Core trendlines for surficial sediment near the mouth of Iron Cove showed that concentrations for 2020 were 330 mg/kg, 297 mg/kg and 750 mg/kg for Cu, Pb and Zn, respectively. To reach twice background levels would take 40 years for Pb and 66 years for Zn at present input rates and Cu showed an increasing trend for this core. Southwest Iron Cove has been dredged and results from the core taken in this area were not useful to predict future metal concentrations.

Temporal changes in surficial sediment concentrations indicate that Cu and Pb declined and Zn increased marginally between 2004 and

2010 in Hen and Chicken Bay, however the core in the south of the bay showed long-term declining trends for all three metals. Core trendlines indicated that the Cu concentration would be 330 mg/kg in 2020 for this area and Pb and Zn concentrations would be at background by this time. The times required for Cu, Pb and Zn to reach two times background level were 13, 6 and 2 years, respectively.

Trendline calculations were not possible in Homebush Bay as no calculated sedimentation rates were available for the core taken during the present study (Taylor et al., 2004). Sedimentation rates are known only for Burns Bay ($0.63 \pm 0.37 \text{ cm yr}^{-1}$) (Taylor et al., 2004) in Lane Cove and in this area Cu and Zn concentrations are increasing at the top of the core. For Cr and Pb, the time to reach two times background is 15 and 40 years, respectively, and Pb concentrations were predicted to be 162 mg/kg by 2020. In Sugarloaf Bay, Middle Harbour, Cr, Cu, Pb and Zn concentrations are predicted to be 238, 284, 309 and 520 mg/kg by 2020, respectively and the time to reach two times background is 76, 92, 73 and 41 years, respectively.

Differences in predicted conditions for 2020 produced using long-term trendlines derived from cores and vintages of surficial sediment data for some sites were due to short-term oscillations in surficial sediment metal concentrations in the recent past. Surficial sedimentary data alone proved to be unreliable when assessing temporal change. However, in combination, the two approaches provided high-resolution temporal trends and a novel vision for environmental change that managers could use with confidence and would find valuable in environmental decision-making and planning.

The time taken for surficial sediment to decline to two times background using trendlines from core data is likely to be considerably longer than that modelled for two reasons. The time required to achieve this objective assumes the rate of change to be constant over time. However, as the concentrations of surficial sediment approaches two times background, the rate of change will slow progressively and the time required to reach this target concentration will increase. Moreover, surficial sediment metal concentration cannot decrease below levels in fluvial material presently being discharged to the water body, which is up to 10–20 times background in some locations in the estuary (Birch and McCready, 2009; Birch, 2011). Concentrations, especially of particulate materials, will need to be reduced substantially to reach target concentrations in sediment mantling the estuary, especially adjacent to stormwater discharge point

Table 7
Normalised metal concentrations (mg/kg) in current and vintage surficial sediment data sets^a.

Embayment		Survey date	n	Co	Cr	Cu	Ni	Pb	Zn
Rozelle Bay & Blackwattle Bay	Mean	2004	10	7.8	79	341	25	576	1097
	Mean	2010	34	7.8	79	432	28	694	1569
	Change	2004–10		0	0	91	3	118	472
Iron Cove	Mean	1975	10	23	92	184	43	371	777
	Mean	2000	45	9.9	91	240	23	505	1072
	Mean	2009	30	9.5	100	269	23	501	1047
Hen and Chicken Bay	Change	2000–09		−0.4	9	29	0	−4	−25
	Mean	1975	10	23	187	423	41	336	711
	Mean	2001	31	9.8	173	430	21	366	824
Homebush Bay	Mean	2004	42	12	168	319	22	320	721
	Mean	2010	39	10	148	317	21	277	735
	Change	2004–10		−2	−20	−2	−1	−43	14
Lane Cove Estuary	Mean	1975	10	28	319	149	50	258	897
	Mean	2004	22	13.4	185	142	33	276	674
	Mean	2010	34	13.5	182	138	32	271	743
Central Middle Harbour	Change	2004–10		0.1	−3	−4	−1	−5	69
	Mean	1999	65	6	64	105	15	168	432
	Mean	2010	32	7.6	71	161	20	220	538
Central Middle Harbour	Change	1999–2010		1.6	7	56	5	48	106
	Mean	1996	107	6	nd ^b	234	22	422	716
	Mean	2010	42	6	88	220	18	274	579
	Change	1996–2010		0	na ^c	−14	−4	−148	−137

^a Cd below detection in most samples.

^b No data.

^c na—not available.

Table 8
Trendline equations and the number of years to reach 2 times background.

		Cr	Cu	Pb	Zn
Blackwattle Bay Core JC-BB-C1	Trendline equation		$y = 1.32x - 598$	$y = 0.12x - 98$	$y = 0.11x - 195$
	R ²	na ^a	0.7779	0.9395	0.9117
	Years to reach EF = 2		60	10	20
Rozelle Bay Core JC-RB-C1	Trendline equation		$y = 0.78x - 429$	$y = 0.08x - 73$	$y = 0.14x - 356$
	R ²	na	0.9731	0.9537	0.9565
	Years to reach EF = 2		23	4	19
Iron Cove Core JC-IC-C12	Trendline equation		$y = 0.44x - 174$	$y = 0.035x - 24$	$y = 0.048x - 74$
	R ²	na	0.5532	0.8639	0.7311
	Years to reach EF = 2		15	20	64
Iron Cove Core JC-IC-C14	Trendline equation		$y = 1.32x - 323$	$y = 0.79x - 376$	$y = 0.35x - 328$
	R ²	na	0.6425	0.8473	0.7755
	Years to reach EF = 2		20	23	20
Iron Cove Core JC-IC-C15	Trendline equation			$y = 0.91x - 353$	$y = 0.64x - 563$
	R ²	na	IT ^b	0.8217	0.4263
	Years to reach EF = 2			40	66
Hen and Chicken Bay Core JC-HC-C10	Trendline equation		$y = 1.03x - 366$	$y = 0.26x - 159$	$y = 0.01x - 56$
	R ²	na	0.75	0.86	0.3
	Years to reach EF = 2		13	6	2
Lane Cove Burns Bay Core 4	Trendline equation	$y = 0.23x - 29$		$y = 0.16x - 32$	
	R ²	0.9572	IT	0.9536	IT
	Years to reach EF = 2	15		40	
Middle Harbour Sugarloaf Bay Core 2	Trendline equation	$y = 0.30x - 80$	$y = 0.26x - 81$	$y = 0.21x - 73$	$y = 0.06x - 39$
	R ²	0.4902	0.4465	0.7602	0.6842
	Years to reach EF = 2	76	92	73	41

^a na = not applicable.

^b IT = Increasing trend at top of core.

sources, e.g. particulate Zn concentrations in stormwater presently being discharged into Iron Cove by Hawthorne Canal (Fig. 3, #3) and Iron Cove Creek (Fig. 3, #4) are 1200 and 1700 mg/kg, respectively. Nevertheless, these predictions allow discharge points to be ranked and prioritised and identify the metals of concern. Introduction of the 'Total Maximum Daily Loads (TMDLs)' concept, as implemented elsewhere (LimnoTech, 2007; Johnson et al., 2007), should be considered a priority for Sydney estuary to reduce surficial sediment metal concentrations to acceptable limits, i.e. twice background levels.

4.6. Metal sources

Contamination levels in Sydney estuary are amongst the highest globally (Birch and Taylor, 1999) and a sound understanding of primary pollutant sources is necessary to formulate estuarine management strategies for this water body (Birch and McCready, 2009). Estuaries receive anthropogenic contributions from point and non-point sources, from urban catchments and from industry, particularly those located on the foreshores (Chapman and Wang, 2001). High fluvial loading, poor flushing (low tidal range and weak tidal currents) and extensive, fine bottom sediment, results in effective entrapment of contaminants close to point sources in the upper regions of embayments in central Sydney estuary (Birch and Taylor, 1999; Cobelo-Garcia and Prego, 2004).

4.6.1. Stormwater

Metals in all six embayments demonstrated strong, declining concentration trends away from fluvial discharge points, which provided strong evidence that catchment stormwater is a major contemporary source of contaminants to Sydney estuary (Fig. 9) (Birch et al., 1996; Birch and McCready, 2009). The source of the majority of metal catchment runoff (ca. 90%) has been attributed to roads and residential property (Birch and Scollen, 2003; Davis, 2010; Beck and Birch, 2011), which comprise >80% of the land-use area in these highly urbanised catchments. Core data indicated increased loading of Cr and Zn into Homebush Bay from Powells Creek, Cu into Burns Bay (Lane Cove) and Cr into Long Bay (Middle Harbour) from stormwater sources.

4.6.2. Parramatta River and the main estuary channel

The distribution of Co and Cr in surficial sediments of Iron Cove and Homebush Bay, Co in Hen and Chicken Bay and Co, Cr, Cu, Pb and Zn in Lane Cove suggested that Parramatta River and the main channel of the estuary are sources of these metals. The concentration of metals at the mouths of these embayments is considerably higher than adjacent to local points of stormwater discharge, whilst contaminant gradients decline into embayments, i.e., the reverse of stormwater distribution trends, which is down estuary (Fig. 9). Surface sediment trends displayed by detailed fingerprinting of dioxin congeners have established that suspended material is moving into embayments from the main channel, providing additional and independent evidence for the main estuary axis as a source of these metals (Birch et al., 2007).

4.6.3. Industrial

Although poor industrial practice has left a large legacy of contamination in Sydney estuary (Birch and Taylor, 2000), sites of contemporary, industry-derived metal contamination observed in the current work were minor. The Pb and Ni dispersion patterns in southeast Homebush Bay and Co on the eastern shoreline of this bay are indicative of metals leaching from remediated industrial sites in the adjacent catchment. Buried legacy contaminants were identified in Blackwattle/Rozelle (Cu, Pb, Ni and Zn), Hen and Chicken (Cu, Pb), Burns (Cr) and Sugarloaf (Cr) Bays in the subsurface of cores. However, these deposits have been overlain by modern, less contaminated surface sediment. The extraordinarily high subsurface concentrations of metals observed in Blackwattle/Rozelle and Hen and Chicken Bays are located well away from stormwater discharge points and suggest that the distribution of metals was very different in times past, compared to the stormwater-dominated patterns observed in modern-day surface sediments.

5. Conclusions

The chemistry of sediments covering Sydney estuary, Australia has been investigated for 35 years and the status of contamination has been well characterised, however temporal trends have remained uncertain.

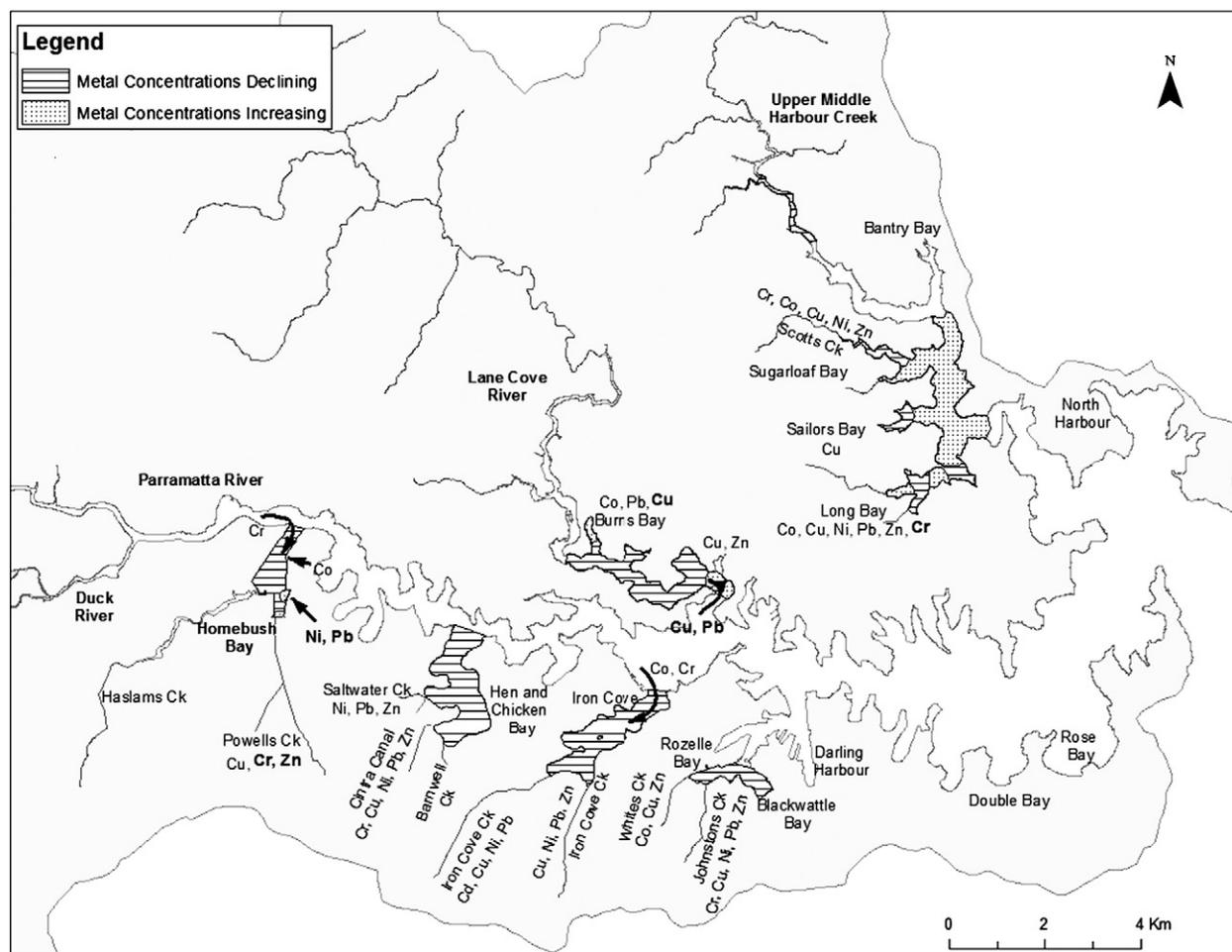


Fig. 9. Summary of temporal trends in surficial sediment metal concentrations and sources of metals.

The major objective of the current investigation was to determine changes in surficial sediment metal concentrations over the historical past and to make predictions of future trends. Traditionally, past contamination trends have been made using sedimentary cores, however core data provided information for one location only and numerous cores are required to provide temporal information over large areas. In the current investigation, a combination of core data and sets of vintage surficial sediment information have been used to spatially extend information on temporal change. Sedimentary cores were also used to determine the pristine condition and magnitude of human-induced change. Core data provided long-term temporal information, which was found to be essential in verifying short-term information derived from vintage surficial sediment datasets and to constrain modelling of future contaminant trends.

The quality of sediment mantling extensive areas of the middle and upper estuaries is improving, whilst some sediment metal concentrations in the lower harbour (Lane Cove and Middle Harbour) are increasing marginally. Small areas of Homebush Bay continue to be impacted by runoff from remediated catchments and metals are entering some off-channel embayments from the central estuary channel. Improvement in sediment quality in the upper estuary may be due to the removal of industry, especially in waterfront locations, together with the implementation of regulation. The declining metal trend is strong in some locations and the time to reach acceptable concentrations (considered in the present work to be two times pre-anthropogenic concentrations) is reasonably short (tens of years). However, these estimations are undoubtedly optimistic as they have been calculated on a straight-line basis from core data and rates of improvement may be expected to slow substantially as the target concentration is approached. In addition, concentrations of

metals presently discharged to Sydney estuary remain high and well above the target concentrations. The introduction of TMDLs for metals should be a priority for Sydney estuary.

The legacy of poor industrial practice is becoming buried with the deposition of less contaminated sediment and the major source of metals to this estuary has changed from industrial to stormwater, with the major contaminant of concern being particle-bound metals, not nutrients or organic compounds (Birch et al., 1999). The main emphasis for management for this estuary should be the control of the quality of incoming stormwater. Retro-fitting remediation devices in old, highly urbanised catchments with minimal spare space, will be difficult and expensive and will require implementation of innovative planning strategies.

Conflict of interest

Authors declare that there is no Conflict of Interest.

Acknowledgements

The authors thank Sarah Corti and Tim Gunns for help in the field and Tom Savage for laboratory assistance.

References

- Abraham GMS, Parker RJ. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ Monit Assess* 2008;136/1-3:227–38.
- Auburn City Council. Environment. Auburn City Council. Sydney: NSW; 2005.

- Beck H, Birch GF. Metals, nutrients and total suspended solids discharged during different flow conditions in highly-urbanised catchments. *Environ Monit Assess* 2011;184/2: 637–53.
- Benoit G, Hemond HF. Evidence for diffusive redistribution of ^{210}Pb in lake sediments. *Geochemica et Cosmochimica Acta* 1991;55:1224–34.
- Birch GF. A test of normalisation methods for marine sediments, including a new post-extraction normalisation (PEN) technique. *Hydrobiologia* 2003;92:5–13.
- Birch GF. A short geological and environmental history of the Sydney Estuary, Australia. In: Birch GF, editor. *Water wind art and debate: how environmental concerns impact on disciplinary research*. Sydney: Sydney University Press; 2007. [Chap 7].
- Birch GF. Contaminated soil and sediments in a highly-developed catchment-estuary system (Sydney estuary, Australia)—an innovative stormwater remediation strategy. *J Soils Sediment* 2011;11/1:194–208.
- Birch GF. Indicators of anthropogenic change and biological risk in coastal aquatic environments. In: Wolenski E, McLusky DS, editors. *Treatise on estuarine and coastal Science, Vol 4*. Waltham: Academic Press; 2012. p. 235–70. [Chap 11].
- Birch GF, McCready S. Catchment condition as a major control on the quality of receiving basin sediments (Sydney Harbour, Australia). *Sci Tot Environ* 2009;407:2820–35.
- Birch GF, O'Hea L. The chemistry of suspended particulate material in a highly contaminated embayment of Port Jackson (Australia) under various meteorological conditions. *Environ Geol* 2007;53:501–16.
- Birch GF, Olmos MA. Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies. *ICES J Mar Sci* 2008;65:1407–13.
- Birch GF, Scollen A. Heavy metals in road dust, gully pots and parkland soils in a highly urbanised sub-catchment of Port Jackson, Australia. *Australian J Soil Res* 2003;41: 1329–42.
- Birch GF, Taylor S. Source of heavy metals in sediments of the Port Jackson estuary, Australia. *Sci Tot Environ* 1999;227:123–38.
- Birch GF, Taylor SE. Distribution and possible sources of organochlorine residues in sediments of a large urban estuary, Port Jackson, Sydney. *Austr J Earth Sci* 2000;47:749–56.
- Birch GF, Taylor SE. Assessment of possible sediment toxicity of contaminated sediments in Port Jackson estuary, Sydney, Australia. *Hydrobiologia* 2002;472: 19–27.
- Birch GF, Taylor SE. Sydney harbour and catchment: contaminant status of Sydney harbour sediments. A handbook for the public and professionals. Published by the Geological Society of Australia, Environmental, Engineering and Hydrogeology Specialist Group; 2004 [101 pp.].
- Birch GF, Evenden D, Teutsch M. Dominance of point source in heavy metal distributions in sediments of a major Sydney estuary (Australia). *Environ Geol* 1996;28:1–6.
- Birch GF, Ingleton T, Taylor SE. Environmental status of the world's largest coal exporting harbour, Port Hunter, Newcastle, Australia. *J Mar Environ Engineering* 1997;4:133–45.
- Birch GF, Eyre BD, Taylor SE. The use of sediments to assess environmental impact of a large coastal catchment—the Hawkesbury River system. *Australian Geol Surv Organ J* 1998;17:193–201.
- Birch GF, Eyre B, Taylor SE. The distribution of nutrients in bottom sediments of Port Jackson (Sydney Harbour), Australia. *Mar Poll Bull* 1999;38:1247–51.
- Birch GF, Harrington C, Symons RK, Hunt JW. The source and distribution of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans in sediments of Port Jackson, Australia. *Mar Poll Bull* 2007;54:295–308.
- Birch GF, McCready S, Long ER, Taylor SE, Spyris G. Contaminant chemistry and toxicity of sediments in Sydney Harbour, Australia: spatial extent and chemistry-toxicity relationships. *Mar Ecol Prog Ser* 2008a;363:71–87.
- Birch GF, Russell AT, Mudge SM. Normalisation techniques in forensic assessment of contaminated environments. In: Ball AS, Mudge SM, editors. *Methods in environmental forensics*. Boca Raton, FL, USA: Taylor and Francis Group; 2008b.
- Birch GF, Murray O, Johnson I, Wilson A. Reclamation in Sydney estuary, 1788–2002. *Australian Geogr* 2009;40(3):347–68.
- Birch GF, Olmos M, Lu XT. Assessment of future anthropogenic change and associated benthic risk in coastal environments using sedimentary metal indicators. *J Environ Manag* 2012;107:64–75.
- Birmingham J, Jack I, Jeans D. Australian pioneer technology. Richmond, NSW, Australia: Heinemann Educational; 1979.
- Butland BD. Heavy metal waste dump to seagrass savannah: a study of the spatio-temporal relationships between seagrass distribution and heavy metal concentrations. Hen and Chicken Bay. School of Geosciences, University of Sydney. Unpubl. BSc thesis (Marine Science), University of Sydney, 2004.
- Carballeira A, Carral E, Puente X, Villares R. Regional scale monitoring of coastal contamination—nutrients and heavy metals in estuarine sediments and organisms on the coast of Galicia (northwest Spain). *Internat J Environ and Poll* 2000;3:534–72.
- Cardoso R, de Fatima Araujo M, da Conceicao Freitas M, Fatela F. Geochemical characterisation of sediments from marginal environments of Lima Estuary (NW Portugal). *Geosciences On-line Journal* 2008;5(6):1–11.
- Chang C-H. Use of sedimentary metal indicators in environmental management of an offchannel embayment (Iron Cove) in Port Jackson, Sydney, Australia. Unpubl. MAppSci thesis, School of Geosciences, University of Sydney, Australia, 2009.
- Chang C-H. Use of sedimentary metals as an indicator of estuarine health in four embayments of Sydney estuary, Australia. Unpubl. MSc thesis, School of Geosciences, University of Sydney, Australia, 2010. p. 87.
- Chang C-H. Use of sedimentary metals as an indicator of estuarine health in four embayments of Sydney estuary, Australia. Unpubl. MSc thesis, School of Geosciences, University of Sydney, Australia, 2011.
- Chapman PM, Wang F. Assessing sediment contamination in estuaries. *Environ Toxicol Chem* 2001;20(1):3–22.
- Chatterjee M, Silva Filho EV, Sarkar SK, Sella SM, Bhattaharya A, Satpathy KK, et al. Distribution and possible source of trace elements in the sediment cores of a tropical macrotidal estuary and their ecotoxicological significance. *Environ Internat* 2007;33: 346–56.
- Churchill L. Assessing the magnitude of human-induced change and biological risk, in the past and in the future in Middle Harbour, Sydney estuary, Australia using sedimentary metal indicators. Unpubl. MAppSci, School of Geosciences, Sydney University, 2011.
- Cobelo-Garcia A, Prego R. Influence of point sources on trace metal contamination and distribution in a semi-enclosed industrial embayment: the Ferrol Ris (NW Spain). *Estuar Coast Shelf Sci* 2004;60:695–703.
- Collett BV. Balmain to city foreshores study: Iron Cove Bridge to Sydney Harbour Bridge, North Ryde: Centre for Environmental Studies. Sydney, Australia: Macquarie University; 1979.
- Das P, Marchesiello P, Middleton JH. Numerical modelling of tide-induced residual circulation in Sydney Harbour. *Mar Freshw Res* 2000;51:97–112.
- Davis B. Investigation of the primary sources of stormwater pollutants in highly urbanised catchments. Unpubl. PhD thesis. School of Geosciences, The University of Sydney, Sydney, Australia; 2010.
- Deely JM, Fergusson JE. Heavy metal and organic matter concentrations and distributions in dated sediments of a small estuary adjacent to a small urban area. *Sci Tot Environ* 1994;153:97–111.
- EOSAN. European Organisation for the Safety of Air Navigation. WGS 84 Implementation Manual; 1998/13.
- ESRI. ArcGIS 9.3 Desktop Help. Redlands, CA, USA: ESRI; 2009.
- Fabris CJ, Monahan CA, Batley GE. Heavy metals in waters and sediments of Port Phillip Bay, Australia. *Mar Freshw Res* 1999;50:503–13.
- Fanou J. Distributions and sources of heavy metals in the Middle Harbour Catchment, Sydney. Unpubl. Graduate Diploma (Environmental Science) thesis, Sydney University, Australia; 1996.
- Forstner U, Wittmann GTW. *Metal pollution in the aquatic environment*. New York: Springer-Verlag; 1979.
- Geyh M, Schleider H. *Absolute age determination: physical and chemical dating methods and their application*. Berlin: Springer Verlag; 1990.
- Grant A, Middleton R. An assessment of metal contamination of sediments in the Humber Estuary, U.K. *Est Coast Shelf Sci* 1990;31:71–85.
- Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G. Assessment of metal mobility in dredged harbour sediments from Barcelona. Spain *Sci Tot Environ* 2004;321: 241–55.
- Hatje V, Rae K, Birch GF. Trace metal and total suspended solids concentrations in freshwater: the importance of small-scale temporal variation. *J Environ Monit* 2001;3:251–8.
- Herbert C. Sydney basin stratigraphy. In: Herbert C, editor. *Geology of the Sydney 1: 100,000 Sheet 9130*. Sydney: New South Wales Department of Mineral Resources; 1983. p. 7–34.
- Hutson P. The use of risk and ecological/conservation value assessments to provide more effective and strategic management of estuarine environments: Port Jackson (Australia): a case study. Unpubl. BSc (Hons) thesis, School of Geosciences, The University of Sydney, Sydney, 2005.
- Irvine IA. Sydney Harbour: sediments and heavy metal pollution. Unpubl. PhD thesis. University of Sydney, Sydney, Australia; 1980.
- Irvine IA, Birch GF. Distribution of heavy metals in surficial sediments of Port Jackson, Sydney, New South Wales. *Australian J Earth Sci* 1998;45(2):297–304.
- Johnson G, Gervino N, Gunderson L, Hotka L, MacGregor M, Vavricka M, et al. Turbidity TMDL protocols and submittal requirements. St. Paul, MN: Minnesota Pollution Control Agency, USA; 2007.
- King C. Determining pre-anthropogenic heavy metal concentrations in estuarine sediments. Unpubl. BSc (Hons) thesis, School of Geosciences, The University of Sydney, Sydney, Australia, 2004.
- Koide M, Bruland KW, Goldberger D. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. *Geochim Cosmochim Acta* 1973;37:1171–87.
- Lawrence M. Modelling atmospheric deposition of vehicular emissions in an Australian urban environment. Unpubl. BSc thesis, School of Geosciences, The University of Sydney, Sydney, Australia, 2005.
- LCEC. An environmental investigation of sediments in the Lane Cove Estuary. Report commissioned by the Lane Cove Estuary Committee. Sydney, Australia: Lane Cove Council by the Environmental Geology Group, School of Geosciences, The University of Sydney; 1999 [October].
- Lee J-H. Use of sedimentary metal indicators to assess temporal change in the contaminant status of Lane Cove sub-estuary. Unpubl. MSc thesis, University of Sydney, NSW, Australia, 2010. p. 89.
- Lee Jung-Ho. Use of sedimentary metal indicators to assess temporal change in the contaminant status of Lane Cove Sub-estuary. Unpubl. MAppSci thesis, School of Geosciences, Sydney University, Australia, 2011.
- Lee SB. Catchment and estuary response to high precipitation in a well-mixed/stratified estuary (Sydney estuary), Australia. Unpubl. PhD thesis, School of Geosciences, The University of Sydney, Sydney, Australia, 2012.
- Lee SB, Birch GF. Utilising monitoring and modelling of estuarine environments to investigate catchment conditions responsible for stratification events in a typically well-mixed urbanised estuary. *J Est Coastal Shelf Sci* 2012;111:1–6.
- Lee SB, Birch GF, Lemcker C. Field and modelling investigations of fresh-water plume behaviour in response to infrequent high-precipitation events, Sydney Estuary Australia. *J Est Coastal Shelf Sci* 2011;92:380–402.
- Legislative Council. Redevelopment and remediation of the Rhodes Peninsula Report 25, June 2002. Standing Committee on State Development, Parliamentary Paper Number 135; 2002.
- LimnoTech. PCB TMDL model for the Potomac River estuary. Final report on hydrodynamic/salinity and PCB transport and fate models. EPA Contract No.

- 68-C-03-041. Work Assignment No. 4-34 Prepared for Battelle by LimnoTech; 2007. [September 28].
- Links F. Historical trends in land use and the chronology of contamination in sediments of Sydney Harbour. Unpubl. BSc thesis, School of Geosciences, The University of Sydney, Sydney, Australia, 1998.
- Loring DH. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES J Mar Sci* 1991;48(1):101–15.
- Lu XQ, Werner I, Young TM. Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay 2005. *Environ Internat* 2005;3:593–602.
- Luoma SN, Phillips DJH. Distribution, variability and impacts of trace elements in San Francisco Bay. *Mar Poll Bull* 1988;19:413–25.
- Maritime NSW. Annual report. Sydney, Australia: NSW Maritime; 2010.
- Matthai C, Birch GF. Detection of anthropogenic Cu, Pb and Zn in continental shelf sediments off Sydney, Australia—a new approach using normalization with cobalt. *Mar Poll Bull* 2001;42(11):1055–63.
- Mayer T. History of anthropogenic activities in Hamilton Harbour as determined from the sedimentary record. *Environ Poll* 1994;96:341–7.
- McCready S, Slee DJ, Birch GF, Taylor SE. The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Mar Poll Bull* 2000;40(11):999–1006.
- McCready S, Birch GF, Taylor SE. The extraction of heavy metals in Sydney Harbour sediments using 1M HCl and 0.05 M EDTA and implications for sediment quality guidelines. *Australian J Earth Sci* 2003;50:249–65.
- McLoughlin LC. Shaping Sydney Harbour: sedimentation, dredging and reclamation 1788–1990s. *Australian Geogr* 2000;31(2):183–208.
- MPR. Aquatic Ecology and Sediment Quality Survey, Long Bay, Middle Harbour. Survey prepared by Marine Pollution Research Pty. Ltd. for Engineering Design Office, North Sydney Council; December, 2005.
- Mudge SM, Birch GF, Matthai C. The effects of grain size and element concentrations in identification of contaminant source. *J Forensic Sci* 2003;4:305–12.
- Muniz P, Danula E, Yannicelli B, Alonso JG, Medina G, Bicego C. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environ Internat* 2004;29:1019–28.
- Nikandrow AL. A history of industry and heavy metal contamination along the southern shoreline and embayments of Port Jackson, New South Wales. Unpubl. MAppSci thesis, School of Geosciences, The University of Sydney, Sydney, Australia, 2000.
- NLWRA. Australian catchment. River and Estuary Assessment 2002, 1. Canberra, Australia: National Land and Water Resources Audit. Federal Government; 2002.
- NSW O E & H. Case study Rhodes Peninsula Sydney Australia. www.sde.nus.edu.au/ACAD/MEM/seminars/180804pres2.pdf 2011. [Accessed].
- NSW Public Works. Long Bay estuary geotechnical investigation. Draft Report MHL700 prepared by NSW Public Works Manly Hydraulics laboratory; 1994 [July].
- O'Connor BH. Correlation between petrol lead additive consumption and atmospheric lead concentrations in Perth, Western Australia. *Atmospheric Environ* 1990;24B(3):413–7.
- Olmos MA, Birch GF. A novel method for measuring anthropogenic change in coastal lake environments. *Environ Sci and Poll Res* 2010;17/2:270–87.
- OzCoast. Estuary assessment framework for non-pristine estuaries Estuary 37 (Port Jackson). National Heritage Trust; 2000.
- Rice J. Environmental health indicators. *Ocean and Coastal Management* 2003;46:235–59.
- Ridgway IM, Price NB. Geochemical associations and post-depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. *Mar Chem* 1987;21:239–48.
- Rojas de Astudillo L, Chang Yen I, Bekele I. Heavy metals in sediments, mussels and oysters from Trinidad and Venezuela. *Revista de Biología Tropical* 2005;53:41–53. [2003].
- Roussiez V, Ludwig W, Probst JL, Monaco A, Bouloubassi I, Buscail R, et al. Sources and sinks of sediment-bound contaminant in the Gulf of Lions (NW Mediterranean Sea): a multi-tracer approach. *Contin Shelf Res* 2006;2:1843–57.
- Roussiez V, Serge H, Ludwig W, Radakovitch O, de Madron XD, Probst L-L, Monaco A, Delsaut N. Impact of oceanic floods on particulate metal inputs to coastal and deep-sea environments: a case study in the NW Mediterranean Sea. *Cont Shelf Res* 2012;45:15–28.
- Roy PS. Quaternary geology. In: Herbert C, editor. *Geology of the Sydney 1:100,000 Sheet, 9130*. Sydney: New South Wales Department of Mineral Resources; 1983. p. 41–84.
- Russell E. Drummoyne: a western suburbs' history from 1794. Sydney, Drummoyne, N.S.W NSW, Australia: Council of the Municipality of Drummoyne; 1982.
- Sabolch M. Hawthorne Canal—the history of Long Cove Creek. Sydney, Australia: Ashfield and District Historical Society Inc.; 2006.
- Simpson SL, Rochford L, Birch GF. Geochemical influences on metal partitioning in contaminated estuarine sediments. *Mar Freshw Res* 2002;53(1):9–17.
- Smith S. Proposed new pollution control legislation in NSW: background and commentary. Sydney, Australia: NSW Parliamentary Library; 1997.
- Sydney Water. The northside storage tunnel Tunks Park and Long Bay, review of environmental factors for proposed works. Sydney: Publ. Sydney Water; 1998 [<http://opac.library.usyd.edu.au/record=b2417918-S4>].
- Szava-Kovats RC. Grain-size normalisation as a tool to assess contamination in marine sediments: Is the 63 µm fraction fine enough. *Mar Poll Bull* 2008;56/4:629–32.
- Taylor SE. The source and remobilization of contaminated sediment in Port Jackson, Australia. Unpubl. PhD thesis. University of Sydney, Sydney, Australia; 2000.
- Taylor SE, Birch GF, Links F. Historical catchment changes and temporal impact on sediment of the receiving basin, Port Jackson, New South Wales. *Australian J Earth Sci* 2004;51:233–46.
- Thiess Services. Case study: SE Homebush Bay lead remediation project. Sydney, Australia: report prepared by Thiess Services Pty Ltd; 2009 [September].
- Thiess Services. Rhodes remediation project. Sydney, Australia: Thiess Services Pty Ltd.; 2010.
- Townsend J. Industrial and urban development in Hen and Chicken Bay, Sydney Estuary, NSW, Australia and impact of contamination on the estuary. Unpubl. Master of Applied Science Thesis, School of Geosciences, Sydney University, Sydney, Australia, 2011.
- Udofia GE, Essien JP, Eduok SI, Akpan BP. Bioaccumulation of heavy metals by yeasts from Qua Iboe estuary mangrove sediment ecosystem, Nigeria. *African J Microbiol Res* 2009;3:862–9.
- Ünlü S, Topçuoğlu S, Alpar B, Kırbazoğlu Ç, Yılmaz YZ. Heavy metal pollution in surface sediment and mussel samples in the Gulf of Gemlik. *Environ Monit Assess* 2008;144:169–78.
- US EPA. Method 200.8 Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry. Cincinnati, Ohio: U. S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory Office of Research and Development; 1994.
- Willoughby City Council. Flat rock gully and bicentennial reserve. Plan of Management, Part 4. Clouston Rpt NS215. Sydney, Australia: Water Management; 1995.
- Willoughby Council. Willoughby City Introduction and summary (Map and key statistics) [Online]. Available: <http://profile.id.com.au/Default.aspx?id=234&pg=101&gid=10&type=enum> [Accessed 17.11.10], 2010.
- Woodward Clyde. Old Naremburn tip, Small Street, Willoughby. Land leachate investigation and surface water monitoring. Report prepared for Willoughby City Council by Woodward Clyde, Sydney, Australia; 1993 [July].
- Yu R, Yuan X, Zhao Y, Hu G, Tu X. Heavy metal pollution in intertidal sediments from Quanzhou Bay. *China J Environ Sci* 2008;20:664–9.
- Zhou F, Guo H, Liu L. Quantitative identification and source apportionment of anthropogenic heavy metals in marine sediment of Hong Kong. *Environ Geol* 2007;53:295–305.
- Zwolsman JGG, Van Eck GTM, Burger G. Spatial and temporal distribution of trace metals in sediments from the Scheldt estuary, South-West Netherlands. *Est Coast Shelf Sci* 1996;43:55–79.