



History of metal contamination in Lake Illawarra, NSW, Australia



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HIGHLIGHTS

- Lake Illawarra has a history of metal contamination.
- Metal concentrations were higher at the site closest to Port Kembla.
- The metals of highest concern were zinc and copper.

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ABSTRACT

Lake Illawarra has a long history of sediment contamination, particularly by metals, as a result of past and current industrial operations and land uses within the catchment. In this study, we examined the history of metal contamination in sediments using metal analysis and ²¹⁰Pb and ¹³⁷Cs dating. The distributions of copper, zinc, arsenic, selenium, cadmium and lead concentrations within sediment cores were in agreement with historical events in the lake, and indicated that metal contamination had been occurring since the start of industrial activities in Port Kembla in the late 1800s. Most metal contamination, however, has occurred since the 1960s. Sedimentation rates were found to be 0.2 cm year⁻¹ in Griffins Bay and 0.3 cm year⁻¹ in the centre of the lake. Inputs from creeks bringing metals from Port Kembla in the north-east of the lake and a copper slag emplacement from a former copper refinery on the Windang Peninsula were the main sources of metal inputs to Lake Illawarra. The metals of highest concern were zinc and copper, which exceeded the Australian and New Zealand sediment quality guideline values at some sites. Results showed that while historical contamination persists, current management practices have resulted in reduced metal concentrations in surface sediments in the depositional zones in the centre of the lake.

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1. Introduction

In Australia, 80% of the population is currently living in areas near estuaries, bays and harbours (Andutta et al., 2013), resulting in significant human impacts on coastal aquatic environments (Harvey and Caton, 2010). Understanding the history of metal inputs in coastal areas is, therefore, important for the protection and management of estuaries and many other coastal features.

The Illawarra region in New South Wales (NSW), Australia, is noted for its abundance of coal and water resources (Eklund, 2002). Wollongong, the regional centre, has become an important industrial centre in Australia with associated environmental problems related to metals released to the environment from the

production of steel, copper refining and burning of coal, such as lead, mercury, cadmium, arsenic, zinc, copper and selenium (Chenhall et al., 1995; Payne et al., 1997).

Lake Illawarra, an estuarine lake situated at the southern end of the City of Wollongong has faced high environmental pressures because of these industrial activities (Chenhall et al., 1995). This lake is in close proximity to Australia's largest steelworks at Port Kembla and is also close to a major copper smelter and refinery, closed in 1995 after almost a century of operation. On the western shores of Lake Illawarra is a coal-fired power station, which has been operating since 1954 with some intermittent periods of closure. In 2009, it was converted to gas-fired power operation. In addition, Lake Illawarra is at the centre of an area of significant residential development (Chenhall et al., 1994).

An effective way to understand the contaminant inputs and sources into lakes is to measure the history of contamination using

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sediment records (Kilby and Batley, 1993; Hollins et al., 2011). Once the history of contamination is reconstructed in the lake, it is then possible to determine how industrialization has affected the area. For convenience, both metals and metalloids in this study will be referred as metals.

In this study, we investigated the patterns of metal accumulation in sediments in Lake Illawarra over the past 80 years, which encompasses the time Port Kembla industry has been in operation. Metal concentration profiles in sediments have been previously measured in Lake Illawarra (Ellis and Kanamori, 1977; Chenhall et al., 1994, 2004; Gillis and Birch, 2006), but there is no information about selenium and arsenic concentrations, major elements found in Australian black coals. In addition, these studies used different dating techniques with limited use of proxies for cross-checking data. This study sought to: (i) measure concentrations of copper, arsenic, selenium, zinc, cadmium and lead in sediment cores, the metals found in Australian coal (Dale, 2006) and released from the existing industries adjacent to the lake; (ii) use ^{210}Pb , ^{137}Cs and sedimentation rates to understand spatial changes in metal concentrations; (iii) understand to what extent the various industries have contributed metals to the lake.

2. Methods

2.1. Historical setting

Lake Illawarra is a coastal lagoon located 10 km south of Wollongong (Fig. 1). It is a relatively shallow lake, with an average depth of 1.9 m and its deepest point being 3.7 m (Yassini and Jones, 1987). The lake is connected to the ocean by a narrow tidal channel approximately 2.4 km long, with a micro-tidal environment and low current velocities resulting in restricted lake-ocean water exchange (Chenhall et al., 1994). This lake was chosen for this study as it is one of Australian estuaries most affected by industries (Chenhall et al., 1994).

The northern hinterland of the lake is the site of the Port Kembla industrial complex (Fig. 1), including Bluescope (BHP) Steel (which started production in 1928), Port Kembla Copper (PKC) refining and smelting plant (which started production in 1910 and closed in August 2003), coal and grain handling facilities, and chemical fertiliser works (Chenhall et al., 2004). The majority of these industries are in close proximity to Lake Illawarra. It has been reported that two creeks draining sub-catchments associated with Port Kembla, Minnegang and Wegit Creeks, may be the source of metals from the industrial complex (Gillis and Birch, 2006). In addition, the Windang Peninsula was the site of a large deposition of copper slag at around 200–500 m from the foreshore of Lake Illawarra (Fig. 1).

Tallawarra Power Station on the western foreshore of the Lake (Fig. 1) commenced operation in 1954, reaching full operation by 1961. At its peak, it had a capacity of 320 MW from four 30 MW and two 100 MW coal burning units. The station closed in 1989, and stood abandoned until 2003, when it was sold by Pacific Power to TRUenergy and recommissioned as a gas-powered combined cycle plant (Energy Australia, 2013). Tallawarra ash dam, located adjacent to Duck Creek, was used as the dumping ground for ash from the power station in the last years of operation between 1983 and 1989 (TRUenergy Tallawarra, 2005).

2.2. Sediment collection

Sediment cores were collected from eight sites in Lake Illawarra based on their proximity to potential metal sources established from previous studies (Chenhall et al., 1994). At each location, two replicate cores were collected in order to obtain average profiles and check that the sediment profiles were not disturbed by collection procedures or by local human activities. Replicate cores were collected at a distance of 1 m apart.

Sediment cores were collected using acid-washed polyvinylchloride (PVC) tubes. After retrieval, the cores were maintained in a vertical orientation and a steel plunger used to push the

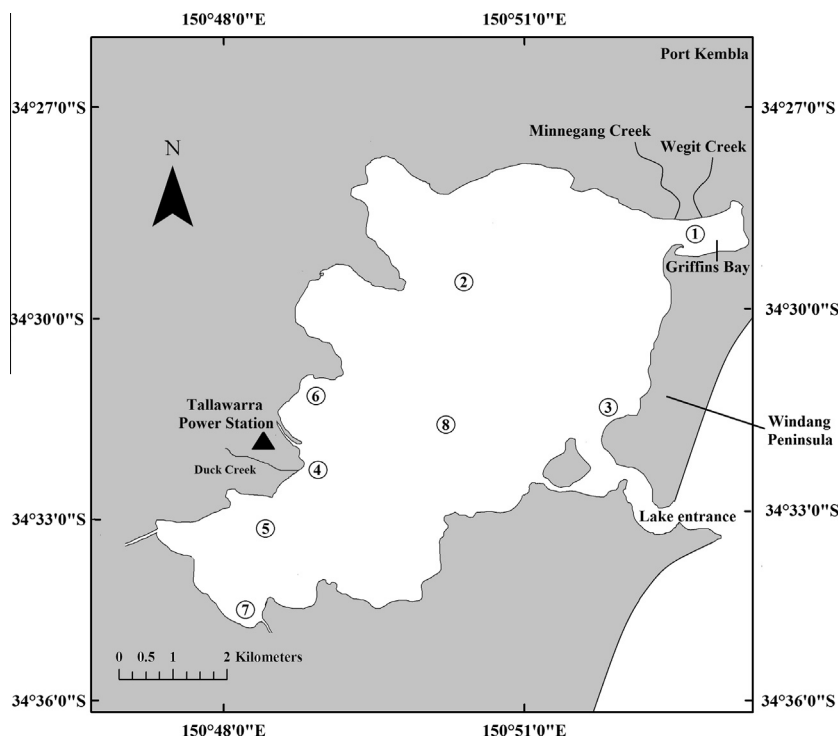


Fig. 1. Sample locations in Lake Illawarra, NSW, Australia. The black triangle represents the location of the Tallawarra Power Station ash dam.

sediment up to the top part of the tube. The 15 cm deep cores were sliced every 3 cm using a stainless-steel spatula and ruler. Sediments were stored in zip-lock plastic bags at 4 °C until analysis.

2.3. Metal analysis

Cores from sites 1 and 8 were chosen for dating analysis as site 1 was expected to reflect Port Kembla inputs and site 8 to reflect deposition of copper slag on the lake foreshore leaching to the lake (Fig. 1).

Prior to metal analysis, all sediment core sections were freeze-dried for 72 h. After drying, samples were placed into 200 mL tubes and homogenization of samples was performed by intensive manual mixing of sediment. Approximately 0.2 g of freeze-dried material was weighed into a 60 mL polytetrafluoroacetate (PTFE) closed digestion vessel (Mars Express) and 2 mL of concentrated nitric acid (Aristar, BDH, Australia) and 1 mL of 30% concentrated hydrochloric acid (Merck Suprapur, Germany) added (Telford et al., 2008). Each PTFE vessel was then capped, placed into a 800 W microwave oven (CEM model MDS-81, Indian Trail, NC, USA), and samples heated at 120 °C for at least 15 min. The diluted digests were cooled to room temperature and diluted to 50 mL with deionised water (Sartorius). The tubes were then centrifuged at 5000 rpm for 10 min. 1 mL of the digest was transferred into a 10 mL centrifuge tube and then diluted to 10 mL with ICP-MS internal standard (Li⁶, Y¹⁹, Se⁴⁵, Rh¹⁰³, In¹¹⁶, Tb¹⁵⁹ and Ho¹⁶⁵). Digests were stored (0–5 °C) until analysis. Samples were analysed for metals using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer DRC-e) with an AS-90 auto-sampler (Maher et al., 2001). Selenium concentrations were cross checked on a Perkin-Elmer 5100 Zeeman graphite furnace atomic absorption spectrometer, with an AS-60 auto-sampler, using a mixture of palladium and magnesium as the matrix modifier (Deaker and Maher, 1995).

For every 36 samples, two CRMs and two blanks were used. The certified reference materials NRC-BCSS1, NRC-Mess1, NIST-1646, NRC-PACS1 were used to check the accuracy of metal analysis. Metal concentrations were in agreement with certified values (Supplementary Table 1).

2.4. Dating analysis

The sediments were dated using ¹³⁷Cs and ²¹⁰Pb methods. The total ²¹⁰Pb activity in sediments has two components: supported ²¹⁰Pb activity (²¹⁰Pb_s) which derives from the decay of in situ radium-226 (²²⁶Ra), and unsupported ²¹⁰Pb activity (²¹⁰Pb_u) which derives from atmospheric fallout. ²¹⁰Pb_s activity is determined indirectly via its grandparent radioisotope ²²⁶Ra. ²¹⁰Pb_u activity was estimated by subtracting ²¹⁰Pb_s activity from the total activity of ²¹⁰Pb (²¹⁰Pb_t) or its progeny polonium-210 (²¹⁰Po).

The in situ production of supported ²¹⁰Pb was measured indirectly from the activity of ²²⁶Ra using gamma spectrometry. Unsupported ²¹⁰Pb_u cannot be measured directly and so was inferred from the activity of total ²¹⁰Pb_t minus the activity of supported ²¹⁰Pb_s. The activity of total ²¹⁰Pb_t was determined by measuring ²¹⁰Pb directly using gamma spectrometry.

Between 20 and 40 g of dried and ground whole sediment was analysed for ¹³⁷Cs, ²¹⁰Pb and ²²⁶Ra activities by Compton suppression gamma spectrometry. The detector system energy calibration was carried out using a National Institute of Standards and Technology (NIST) traceable multi-nuclide standard source and the detector system efficiency calibration was determined using IAEA reference materials including RGU-1, RGTh-1, RGK-1 and Soil-6.

Both the Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models of ²¹⁰Pb dating (Appleby and Oldfield, 1992) were used to construct chronologies for each of the sites, using the ¹³⁷Cs date as a reference point. Inflections in the ²¹⁰Pb_u activities profile usually reflect changes in sediment accumulation rate or bioturbation (Krantzberg, 1985). For those sites where the weight accumulation rate is fairly constant, i.e. where ²¹⁰Pb_u activity monotonically decreases with depth, the CIC and CRS models are usually in agreement. Where there is a non-monotonic trend in the ²¹⁰Pb_u depth profile, the use of the CIC model is usually precluded and the CRS model is used to calculate the chronology.

2.5. Grain size analysis

As the surface area of sediments is grain-size dependent and controls the adsorption of metals, metal concentrations were normalised to grain size in order to interpret metal concentrations in sediments between areas (Blomqvist et al., 1992; Hanson et al., 1993).

All sections of all cores were analysed for sediment grain size at the Australian Nuclear Science and Technology Organisation. Samples were first sieved to the particle size of <2000 μm (i.e. gravel-free) and, sediment fractions were determined using laser detection on a Malvern Mastersizer 2000 with a 300RF lens, 0.05–900 μm. Samples were dispersed in water and 30 s of ultrasonication was used to break up agglomerated particles. A total of three measurements were made for each sample and the average used as the final value. The distribution abundances within the 0.2–2000 μm grain size range were calculated by the Malvern built-in software.

All sediments were classified to four classes: clay (particles with diameter <2 μm), silt (2–20 μm), fine sand (20–200 μm) and coarse sand (200–2000 μm). This classification was developed by McKenzie et al. (2000) and Carlile et al. (2001) to generate soil attribute surfaces for the Australian Soil Resource Information System.

In this study, normalisation of metal concentrations in sediments was performed using iron (Fe) following the method of Suh and Birch (2005). In this process of normalisation, the correlation between iron concentration and fine fraction (silt and clay) was the basis for normalisation. Clay content (<20 μm) significantly predicted iron concentration in total sediment (grain size <2000 μm) (slope = 225.2, *t* (33) = 4.14, *p* < 0.001). Clay content percentage explained 34% of variance in iron concentrations in total sediments (*R*² = 0.34, *F*(1,33) = 17.22; *p* < 0.001; Supplementary Fig. 1). Iron concentrations were corrected to the clay content by using the regression Eq. (2):

$$\text{Normalised Fe} = 8820 + (2252 \times \text{clay content}) \quad (2)$$

Metal concentration values in the sediment were normalised by multiplying a given metal concentration value by 10000 and dividing by the iron-normalised value. Normalised data were only used for comparisons of metal concentrations between sites. As grain size did not significantly change vertically within a core, the original non-normalised data were used in the interpretation of dating data in this study.

2.6. Statistical analysis

To compare the pattern of metal concentrations by sites and by sediment depths, a dissimilarity matrix was built and samples were tested using an Analysis of Similarities Test (ANOSIM) (Clarke, 1993). ANOSIM explicitly compares the level of similarity found in all pairs within each level of a factor against the similarity found in between-level pairs. Significance testing used randomizations (Legendre and Legendre, 2012).

Specifically, this procedure was used to test the null hypothesis that there is no difference in metal concentrations in sediments between sites. If the p -value was less than 0.05, then the null hypothesis was rejected and a t -test pairwise with Bonferroni correction was conducted at the level 0.05 based on dissimilarity ranks.

To visualise similarity between sites, multidimensional scaling (MDS) based on Euclidean distances was used.

All computations were performed using the software R (R Development Core Team, 2013), using the package Vegan (version 2.0-7; URL: <http://cran.r-project.org/web/packages/vegan/index.html>). The graphs of profile cores were built using package Analogue (version 0.10-0; <http://cran.r-project.org/web/packages/analogue/index.html>) and package Lattice (version 0.20-15 <http://cran.r-project.org/web/packages/lattice/index.html>).

3. Results

3.1. Metal concentration variation with depth

Metal concentrations within sediment cores of the lake varied similarly within depth, except for site 1 which had great variability in metal concentration patterns with depth (Fig. 2).

Based on metal background concentrations previously reported for Lake Illawarra of Zn < 87 mg kg⁻¹, Cu < 39 mg kg⁻¹, Cd < 1 mg kg⁻¹ and Pb < 19 mg kg⁻¹ (Ellis and Kanamori, 1977; Gillis and Birch, 2006), in this study, non-normalised concentrations of copper, zinc and lead reached background concentrations within the sampled depth in cores from sites 2, 3 and 4 and cadmium reached background concentrations at all sites, except site 1 (Table 1). If considering background values in other nearby estuarine lakes (e.g. Lake Macquarie, Batley, 1987) of <1 mg Se kg⁻¹ and <15 mg As kg⁻¹, selenium reached background concentrations in the cores from sites 1, 3, 4, 5 and 6, while arsenic reached background concentrations in cores from sites 1 to 7 (Table 1).

3.2. Metal concentrations between sites

The variation in metal concentrations between sites was clear and well defined (Figs. 2 and 3).

Dissimilarity rankings of normalised metal concentrations in sediment cores showed that there was a significant difference in metal concentrations between sites ($R = 0.57$, $p = 0.001$). Pairwise comparisons (Table 2) and the MDS plot (Fig. 3) showed that site 1 was clearly different from the other sites, with higher metal concentrations. Site 3 had a peculiar trend in its metal concentration depth profile, but had concentrations similar to other sites with the exception of site 1.

3.3. History of anthropogenic metal contamination

3.3.1. Lake Illawarra core 1 replicate 1 (core 1.1)

Unsupported ²¹⁰Pb activities for this core from Griffins Bay (Fig. 1) exhibited a decreasing profile with increasing depth (Fig. 4, Table 3). The calculated CIC and CRS model sediment ages were in agreement (Table 3). ¹³⁷Cs activities were higher in the top 9 cm of the core (Table 3). Below 9 cm ¹³⁷Cs activity dropped to 0.6 Bq kg⁻¹. According to the ²¹⁰Pb chronology, the sediment layer at 6–9 cm was 46 years old, and the sediment at 9–12 cm was 65 years old. The low activity of ¹³⁷Cs detected below 9 cm may be a result of ¹³⁷Cs being mobile in the sediment core material. Otherwise the ¹³⁷Cs activities supported the ²¹⁰Pb chronologies.

Based on ²¹⁰Pb results, this core had a constant sedimentation rate of 0.2 cm year⁻¹ and showed a decrease in metal concentrations from the deepest 1927 to 1945 year old sediment layer to

the 6–9 cm layer, which corresponded to 1964–1982 (Fig. 4, Table 3). Metal concentrations then started to increase reaching a maximum at the 3–6 cm layer, which corresponded to 1982–2001. With the exception of arsenic and cadmium, metal concentrations decreased in the top layer which corresponded to 2001–2010.

3.3.2. Lake Illawarra core 8 replicate 2 (core 8.2)

Unsupported ²¹⁰Pb activities for this core from the central area of the lake (Fig. 1) exhibited a decreasing profile with increasing depth (Fig. 5, Table 3). The unsupported ²¹⁰Pb activity at 12–15 cm was still relatively high (Table 3), thus more samples should be analysed below 15 cm until unsupported ²¹⁰Pb reached close to the background level. For this reason the CIC model ²¹⁰Pb dating ages were more accurate than the CRS model ages (Table 3). Significant levels of ¹³⁷Cs activity were detected in all the layers between 0 and 15 cm (Table 3), an indication that the sediment down to 15 cm had accumulated post the nuclear testing. At 12–15 cm, the CIC sediment age was 40 years old, therefore the ¹³⁷Cs activities for this core support the CIC model ²¹⁰Pb chronology.

Based on ²¹⁰Pb results, this core had a constant sedimentation rate of 0.3 cm year⁻¹ and showed a decrease in metal concentrations from the bottom 12–15 cm layer to the mid 9–12 cm, corresponding to 1978 to 1987 (Fig. 5). Metal concentrations then started to increase reaching a maximum at 6–9 cm, corresponding to 1987 to 1997 and slightly decreased again in the top sediment layer, with the exception of selenium which continued increasing and reached its maximum concentration at 3–6 cm corresponding to 1997 to 2006, followed by a decrease in the top sediment layer.

4. Discussion

Our results showed that metal contamination has been occurring in this lake since the start of industrial activities in Port Kembla in the late 1800s (Figs. 4 and 5). Although contamination from Port Kembla started in the late 1800s, most metal contamination occurred from the 1960s.

Although the number of core replicates is low, the unsupported ²¹⁰Pb had a steadily decreasing profile with increasing sediment depth, indicating that cores were not mixed and metal concentration profiles and sedimentation rates were well preserved. The general consistency in metal concentrations in core profiles between replicates (Fig. 2) indicated that core sediments were representative of the area they were sampled from, but caution should be taken when assessing site 1, the location with highest metal concentrations, where there was disagreement between replicates (Fig. 2).

4.1. Metal concentration variation with depth

Metal concentrations in cores only reached background values within the sampled depth at sites 2, 3 and 4. Background metal concentrations in Lake Illawarra sediments were determined by Gillis and Birch (2006) and Ellis and Kanamori (1977) by calculating the mean concentration of metals in the fine fraction from the pre-anthropogenic section of sediment cores, which was assumed to be where the metal concentrations declined to a consistent minimum. Background metal concentrations in Lake Illawarra determined by their method were Zn < 87 mg kg⁻¹, Cu < 39 mg kg⁻¹, Cd < 1 mg kg⁻¹ and Pb < 19 mg kg⁻¹. Copper background values for Lake Illawarra were double than background concentrations in other estuaries in the region (≈17 mg kg⁻¹). Background sediment copper concentrations may be the result of naturally high concentrations of copper in the Gerringong Volcanics, located in

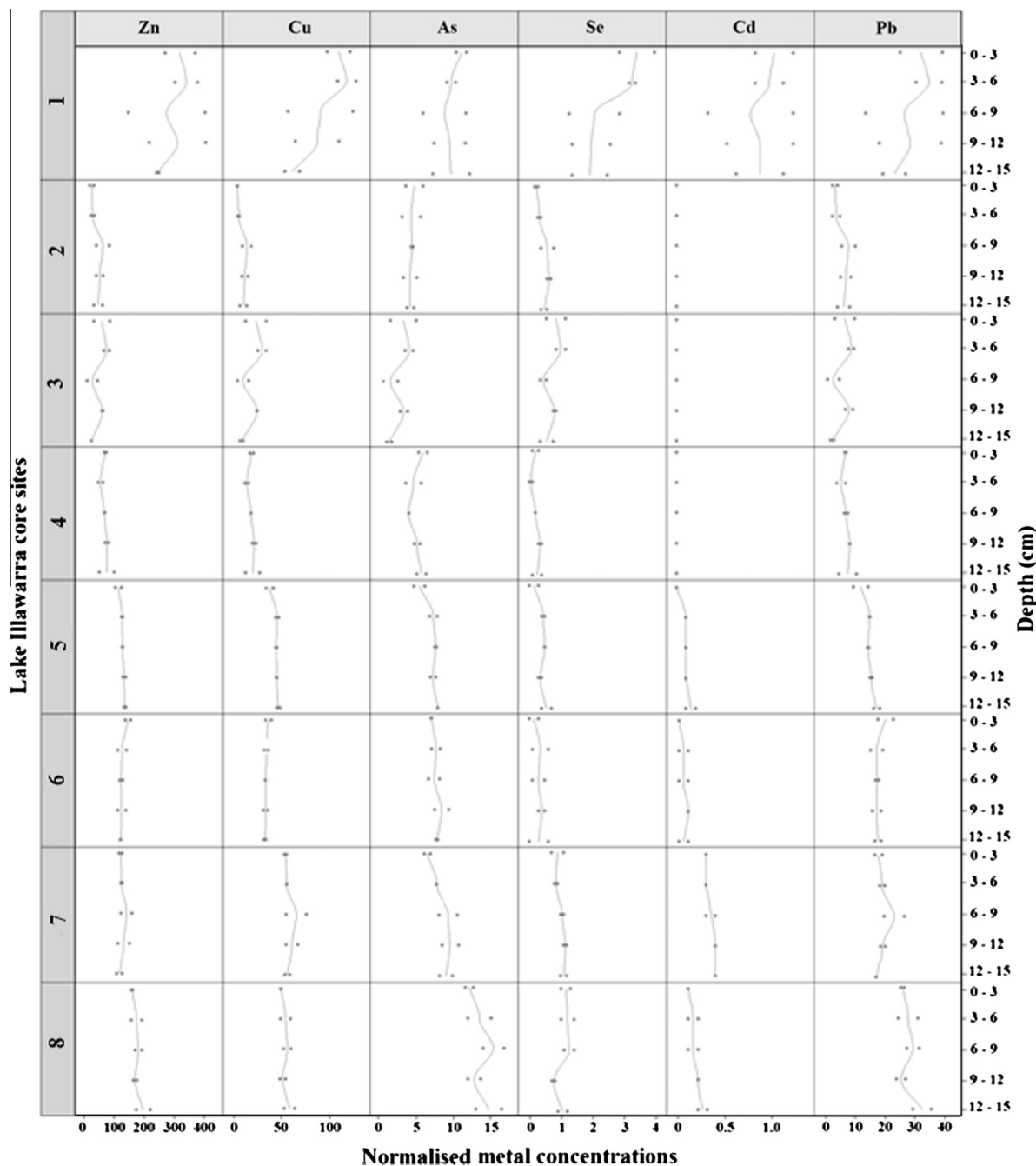


Fig. 2. Profiles of normalised metal concentrations within sediment cores of Lake Illawarra by collection sites. Dots represent the two replicate cores collected per site and lines represent the average metal concentration between replicates. No lines indicate that metal concentrations are below detection limits.

the catchment (Carr, 1984; Zhou, 1985; Carballeira et al., 2000; Smith, 2001). Selenium concentrations did not reach background concentrations at sites 2, 7 and 8, and neither did arsenic concentrations at site 8 (Table 1).

No metal reached background concentration values at site 1 as a result of Port Kembla long-term industrial discharges which started in the beginning of the 1900s, in agreement with previous studies. The oldest study of metal concentration profiles in Lake Illawarra cores is by Ellis and Kanamori (1977), who collected samples in the 1970s. Their results agree with later results, and deposition during the subsequent 20 years shifted background values to about 5 cm deeper when Chenhall et al. (1994), Payne et al. (1997) and Gillis and Birch (2006) collected their cores. A different result,

though, was obtained by Chenhall et al. (1994) who reported metal concentrations in two cores of 1 m depth. Their results showed that zinc, copper and lead background concentrations were found at about 60 cm depth. Depths at which maximum concentrations were found were different for each element, with the zinc maximum concentrations at around 10–15 cm, copper maximum concentrations at around 50 cm while lead concentrations had different maxima in each core. One core, as for the other elements, had a lead concentration maximum at around 25 cm, while, in the second core, an initial maximum at 88 cm was followed by another maximum at 25 cm. This initial maximum was not recorded in previous published work probably because of limitations (60 cm) in core lengths. It is conceivable that the elevated lead concentrations

Table 1
Whole sediment metal concentrations (mg kg⁻¹) and normalised metal concentrations by depth of cores from sites 1 to 8.

Site		Metals (mg kg ⁻¹)												Grain size (%)					
Core	Depth (cm)	Fe	Fe Norm	Zn	Zn Norm	Cu	Cu Norm	As	As Norm	Se	Se Norm	Cd	Cd Norm	Pb	Pb Norm	Clay <2 µm	Silt 2–20 µm	Sand 20–200 µm	Coarse sand 200–2000 µm
1.1	0	9780	18500	284	154	101	54.5	11.4	6.2	2.8	1.5	0.9	0.5	28.4	15.4	14	29	41	17
	3	11600	16800	317	189	111	66.0	10.1	6.0	3.1	1.8	0.9	0.5	33.9	20.2	12	24	55	10
	6	6720	13200	162	123	60	45.6	6.9	5.2	1.2	0.9	0.4	0.3	17.0	12.9	6	13	59	22
	9	7500	12900	232	179	67.5	52.3	8.4	6.5	1.3	1.0	0.6	0.5	21.4	16.6	7	11	44	38
	12	7330	9740	264	271	56.5	58	8.2	8.4	1.3	1.3	0.7	0.7	22.8	23.4	1	3	35	61
1.2	0	14200	15900	385	243	124	78.1	12.8	8.1	3.9	2.5	1.3	0.8	42.6	26.9	0	31	56	13
	3	14400	17500	394	225	130	74.1	11.3	6.4	3.3	1.9	1.2	0.7	42.4	24.2	1	38	55	6
	6	15400	18100	417	231	127	70.3	12.7	7.0	2.8	1.5	1.3	0.7	42.8	23.7	1	40	53	6
	9	14100	18000	419	233	113	62.6	12.6	7.0	2.5	1.4	1.3	0.7	42.3	23.5	1	40	53	6
	12	12100	17400	256	147	72.2	41.5	13.2	7.6	2.4	1.4	1.2	0.7	30.3	17.4	1	37	53	9
2.1	0	4350	9490	26	27	4.0	4.2	7.0	7.4	0.2	0.2	0	0	5.3	5.6	0	3	5	92
	3	5000	9540	28	29	6.3	6.6	6.6	6.9	0.2	0.2	0	0	6.0	6.3	0	3	12	85
	6	5050	11300	35	31	9.0	8.0	5.4	4.8	0.3	0.3	0	0	6.6	5.9	1	10	15	75
	9	7080	13700	58	42	14.7	10.7	6.1	4.4	0.6	0.4	0	0	9.8	7.1	1	20	23	55
	12	6710	15300	55	36	13.7	9.0	5.7	3.7	0.3	0.2	0	0	9.4	6.2	2	27	21	51
2.2	0	2890	9850	13	13	3.4	3.5	4.6	4.7	0.1	0.1	0	0	3.6	3.7	0	4	7	89
	3	2970	9600	15	16	4.0	4.2	4.1	4.3	0.3	0.3	0	0	3.6	3.7	0	3	11	86
	6	8120	16900	78	46	18.8	11.2	5.6	3.3	0.7	0.4	0	0	11.2	6.6	2	34	23	42
	9	4880	12300	35	29	8.4	6.8	4.3	3.5	0.5	0.4	0	0	6.3	5.1	1	14	18	67
	12	3780	13200	26	20	6.7	5.1	4.8	3.6	0.5	0.4	0	0	5.2	4.0	1	18	18	63
3.1	0	2220	13450	32	24	12.7	9.4	2.3	1.7	0.4	0.3	0	0	4.2	3.1	0	20	21	58
	3	5810	17600	83	47	34.7	19.7	5.4	3.1	1.0	0.6	0	0	10.6	6.0	1	38	40	21
	6	737	11000	10	9	4.7	4.3	1.3	1.2	0.2	0.2	0	0	1.7	1.5	0	10	19	71
	9	4090	15300	59	39	24.9	16.3	3.6	2.4	0.6	0.4	0	0	10.1	6.6	1	28	36	36
	12	1980	12600	24	19	10.7	8.5	2.5	2	0.6	0.5	0	0	3.8	3.0	0	16	22	62
3.2	0	5910	13900	86	62	34.6	24.9	5.8	4.2	1.0	0.7	0	0	10.8	7.8	0	22	29	49
	3	4240	17300	65	38	25.9	15.0	4.3	2.5	0.7	0.4	0	0	8.8	5.1	1	37	40	22
	6	2860	13400	45	34	16.2	12.1	3.3	2.5	0.4	0.3	0	0	5.6	4.2	0	20	27	53
	9	4370	16700	62	37	24.7	14.8	4.6	2.8	0.7	0.4	0	0	7.7	4.6	1	34	38	27
	12	1470	14300	24	17	7.3	5.1	1.8	1.3	0.2	0.1	0	0	2.8	1.9	0	24	30	46
4.1	0	8170	17100	65	38	19.0	11.1	6	3.5	0.1	0.1	0	0	8.5	5.0	2	35	13	51
	3	5450	18400	38	21	10.6	5.7	4.2	2.3	0.1	0.1	0	0	5.4	2.9	2	41	17	40
	6	7260	21300	59	28	16.8	7.9	4.6	2.2	0.2	0.1	0	0	7.8	3.7	2	53	17	27
	9	8610	18300	75	41	21.8	11.9	5.4	2.9	0.3	0.2	0	0	9.7	5.3	3	40	16	42
	12	10500	16600	92	55	25.8	15.6	7.0	4.2	0.4	0.2	0	0	12.1	7.3	2	32	13	53
4.2	0	7630	17100	58	34	15.7	9.2	7.1	4.1	0.3	0.2	0	0	8.1	4.7	2	35	15	48
	3	7280	19300	54	28	14.4	7.5	6.3	3.3	0	0	0	0	8.3	4.3	3	44	12	41
	6	7140	17500	60	34	16.8	9.6	4.6	2.6	0.2	0.1	0	0	9.2	5.2	3	36	15	47
	9	7860	23800	61	25	17.9	7.5	6.1	2.6	0.4	0.2	0	0	9.8	4.1	4	63	14	19
	12	6260	17300	44	25	11.2	6.5	5.7	3.3	0.1	0.1	0	0	6.0	3.5	2	35	11	51
5.1	0	12400	18700	99	53	35.9	19.2	5.1	2.7	0.3	0.2	0	0	11.6	6.2	2	42	49	8
	3	16300	19300	122	63	49.0	25.3	8.3	4.3	0.4	0.2	0.1	0.1	17.2	8.9	2	45	51	2
	6	16300	20500	121	59	47.3	23.0	8.0	3.9	0.5	0.2	0.1	0	16.3	7.9	2	51	46	2
	9	16400	21400	133	62	47.5	22.1	7.4	3.5	0.4	0.2	0.1	0	17.1	8.0	3	53	43	1
	12	15800	22200	128	58	47.0	21.1	8.4	3.8	0.4	0.2	0.2	0.1	18.4	8.3	3	57	39	1
5.2	0	14500	20100	118	59	43.4	21.6	6.6	3.3	0	0	0	0	16.5	8.2	2	49	48	2
	3	15100	19600	119	61	45.8	23.3	7.3	3.7	0.5	0.3	0.1	0.1	16.9	8.6	2	46	50	2
	6	15500	20400	123	61	46.2	22.7	8.2	4	0.5	0.2	0.1	0	16.8	8.2	2	49	47	2
	9	15600	20700	122	59	46.8	22.7	8.1	3.9	0.3	0.1	0.1	0	18.0	8.7	3	50	43	4
	12	16300	21200	132	63	50.1	23.7	8.4	4	0.7	0.3	0.1	0	20.4	9.6	3	52	43	2
6.1	0	14400	24500	138	57	35.8	14.6	7.7	3.1	0	0	0	0	20.0	8.2	4	66	22	9
	3	15200	23300	143	61	38.8	16.7	9.0	3.9	0.1	0	0	0	21.6	9.3	5	59	25	11
	6	14000	23900	131	55	35.3	14.8	7.4	3.1	0.1	0	0	0	19.3	8.1	6	61	27	7
	9	14600	23900	141	59	38.6	16.2	10.1	4.2	0.3	0.1	0.1	0	21.0	8.8	4	63	24	9
	12	13600	23500	123	52	34.0	14.4	8.4	3.6	0	0	0	0	19.0	8.1	5	61	24	10
6.2	0	16200	27500	157	57	41.9	15.2	7.8	2.8	0.3	0.1	0	0	25.1	9.1	3	80	17	1
	3	14700	23500	114	49	34.8	14.8	7.8	3.3	0.6	0.3	0.1	0	17.6	7.5	4	61	26	10
	6	15600	23500	120	51	35.8	15.3	8.9	3.8	0.5	0.2	0.1	0	20.2	8.6	5	60	25	10
	9	14300	23700	114	48	33.1	14.0	8.2	3.5	0.5	0.2	0.1	0	18.2	7.7	4	62	24	11
	12	15600	23200	125	54	36.2	15.6	8.6	3.7	0.6	0.3	0.1	0	21.1	9.1	5	59	25	11
7.1	0	14300	21600	110	51	52.4	24.3	6.8	3.1	1.2	0.6	0.3	0.1	18.0	8.3	2	55	42	2
	3	15400	22200	117	53	54.9	24.8	8.5	3.8	1.0	0.5	0.3	0.1	19.6	8.8	3	57	40	0
	6	21600	22800	154	68	75.3	33.0	11.4	5.0	1.2	0.5	0.4	0.2	27.9	12.2	3	60	37	1
	9	16200	22200	106	48	54.1	24.4	9.2	4.1	1.2	0.5	0.4	0.2	19.8	8.9	3	56	40	1
	12	15400	22200	103	46	52.6	23.7	8.9	4.0	1.3	0.6	0.4	0.2	18.3	8.2	3	57	35	5

(continued on next page)

Table 1 (continued)

Location		Metals (mg kg ⁻¹)												Grain size (%)					
Site core	Depth (cm)	Fe	Fe Norm	Zn	Zn Norm	Cu	Cu Norm	As	As Norm	Se	Se Norm	Cd	Cd Norm	Pb	Pb Norm	Clay <2 μm	Silt 2–20 μm	Sand 20–200 μm	Coarse sand 200–2000 μm
7.2	0	15400	22800	121	53	55.0	24.1	7.6	3.3	0.8	0.4	0.3	0.1	20.4	8.9	2	61	38	1
	3	16100	21400	121	57	55.0	25.6	8.5	4.0	0.9	0.4	0.3	0.1	21.2	9.9	4	52	43	1
	6	15900	22900	117	51	54.4	23.7	8.8	3.8	1.1	0.5	0.3	0.1	21.0	9.2	3	60	37	1
	9	20500	22800	145	64	66.5	29.1	11.5	5.0	1.3	0.6	0.4	0.2	21.4	9.4	3	59	37	0
	12	18900	23000	120	52	57.9	25.1	10.7	4.6	1.1	0.5	0.4	0.2	18.4	8.0	3	60	36	1
8.1	0	20700	27200	166	61	48.0	17.7	13.8	5.1	1.3	0.5	0.1	0	28.0	10.3	3	79	17	2
	3	21000	27100	166	61	47.4	17.5	13.0	4.8	1.0	0.4	0.1	0	26.1	9.6	4	77	17	2
	6	22200	27500	177	64	50.6	18.4	15.1	5.5	1.4	0.5	0.1	0	28.9	10.5	5	78	15	2
	9	21100	27800	185	67	52.1	18.8	14.8	5.3	0.8	0.3	0.2	0.1	28.4	10.2	5	79	15	1
	12	20500	27600	182	66	51.1	18.5	14.1	5.1	1.2	0.4	0.2	0.1	30.9	11.2	5	79	16	1
8.2	0	20500	28600	170	60	47.4	16.6	12.7	4.4	1.0	0.3	0.1	0	26.9	9.4	15	73	12	0
	3	24100	28900	200	69	57.6	19.9	16.2	5.6	1.4	0.5	0.2	0.1	32.7	11.3	15	74	11	0
	6	24100	26900	200	74	57.8	21.5	17.9	6.7	1.1	0.4	0.2	0.1	33.1	12.3	14	67	17	3
	9	19300	27400	172	63	46.5	17.0	13.0	4.7	0.7	0.3	0.2	0.1	25.5	9.3	15	68	11	6
	12	26100	28500	229	80	61.8	21.7	17.6	6.2	0.9	0.3	0.3	0.1	37.2	13	15	73	12	1

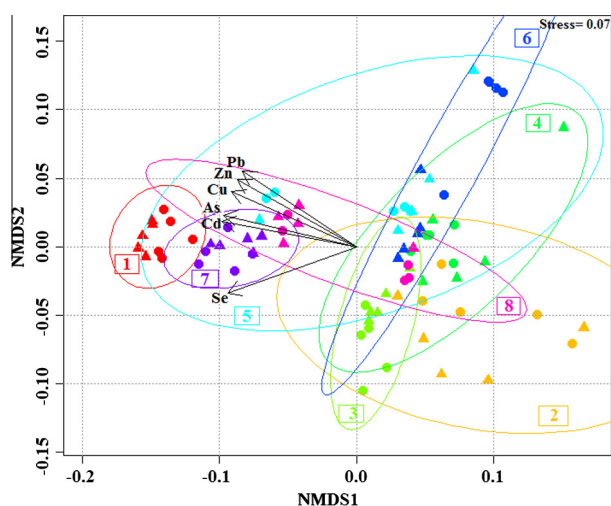


Fig. 3. MDS plot showing between-site similarity in metal concentrations in sediments from Lake Illawarra. Plot based on data for eight original cores (circles) and eight replicates (triangles), with points colour coded for sites. Arrows represent the relative contribution of the original variables to the variability along the first two MDSs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Pairwise comparisons of metal dissimilarity ranks between cores from Lake Illawarra.

Sites	Between	1	2	3	4	5	6	7
1	..	–	–	–	–	–	–	–
2	–	–	–	–	–	–
3	0.0023	...	1	–	–	–	–	–
4	1	0.4	–	–	–	–
5	0.1	–	–	–
6	0.4	1	–	–
7	1	...	1	1	1	–
8	1	...	1	1	1	1

* <0.05.

** <0.01.

*** <0.001.

in the deeper cores reflect the inputs of the first industrial activities (lead smelting in 1896). An alternative hypothesis, involving mobilisation of lead down the sediment column, does not appear to be feasible, given the sharply defined nature of lead enrichment, unless, a change in physicochemical factors resulted in lead fixation at specific depths.

4.2. Metal concentrations between sites

Site 1 at Griffins Bay (Fig. 1) showed the most enrichment in metal concentrations within cores (Fig. 2). This was the site that best reflected historical industrial activities as metal concentration changes in cores (Figs. 2 and 3). The high concentrations of metals in sediments at this site next to Port Kembla confirm that this industrial complex is an important source of metals, which is in agreement with previous studies (Roy and Peat, 1976; Ellis and Kanamori, 1977; Chenhall et al., 1994; Payne et al., 1997; Chiaradia et al., 1997; Gillis and Birch, 2006). An explanation for this discharge of metals has been given by Gillis and Birch (2006) who reported that sediment in Minnegang and Wegit Creeks discharging into Griffins Bay contained higher metal concentrations than sediments mantling Griffins Bay, suggesting that these creeks are the source of metals to the embayment. These creeks drain sub-catchments associated with urban areas adjacent to Port Kembla. Beavington (1973) reported elevated concentrations of acetic acid-extractable zinc (103 mg kg⁻¹), lead (17 mg kg⁻¹), cadmium (1.0 mg kg⁻¹), and EDTA-extractable copper (488 mg kg⁻¹), in soils from urban areas adjacent to Port Kembla, suggesting that top soil erosion may be a source of metals to the creeks. Water exchange between Griffins Bay and the main body of the lake is usually limited by a sub-aqueous spit (Clarke and Eliot, 1984) thus Griffins Bay acts as a sink for sediments and associated metals entering the embayment.

Site 8 at the Windang Peninsula, where copper slag containing zinc, copper, lead and cadmium was dumped, had slightly elevated concentrations of arsenic and lead relative to sites 2–7, but no evidence of copper and cadmium enrichment.

Distinctively higher metal concentrations at site 1 in Griffins Bay sediments compared with the rest of Lake Illawarra, suggest that direct atmospheric deposition of metals is not the main mechanism governing metal distribution in the lake. Had atmospheric contributions been the dominant source of metals to the lake, metal concentrations would show a uniform gradient across the northern part of the lake, which was not evident from the data collected in the current work. Inputs from creeks in the northeast, as reported by Gillis and Birch (2006), appear to be more important in determining spatial metal concentration patterns than atmospheric processes.

4.3. Sedimentation rates

The sedimentation rates give an indication of lake dynamics and sediment movement (Tylmann, 2004). In Lake Illawarra,

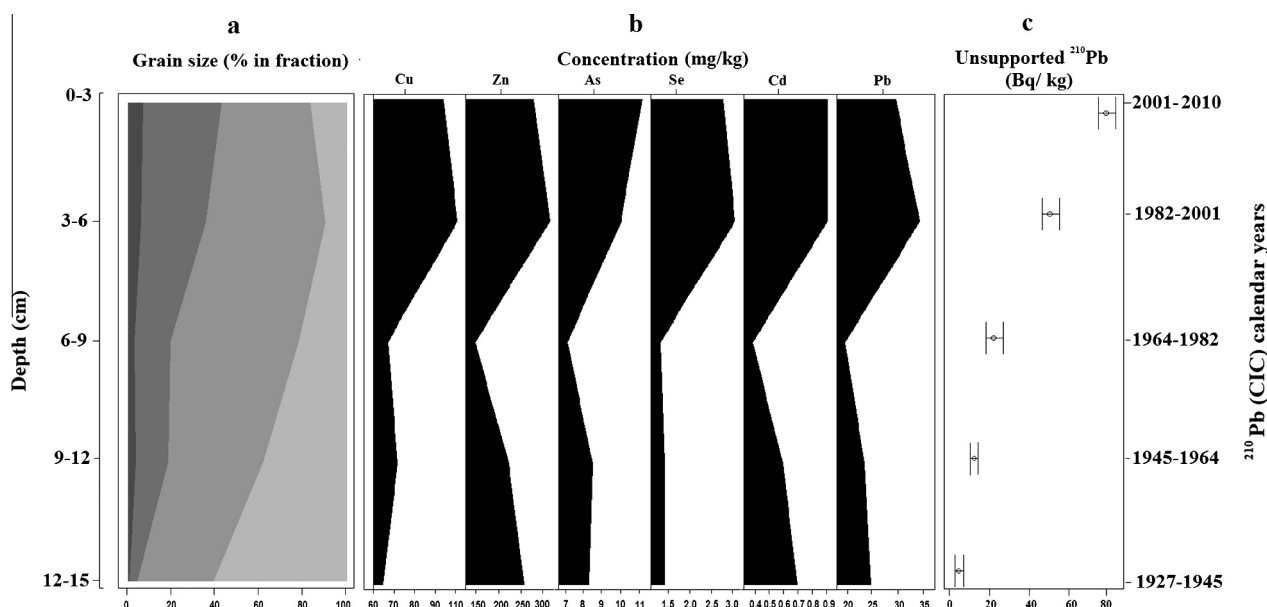


Fig. 4. Lake Illawarra (core 1.1) depth profiles of (a) grain size distributions with depth; dark grey % clay (<2 μm), medium grey % silt (2–20 μm), grey % fine sand (20–200 μm), light grey % coarse sand (200–2000 μm), (b) total metal concentration and (c) ^{210}Pb activity depth profile.

Table 3
 ^{137}Cs , ^{210}Pb dating, sedimentation rate (mean ± uncertainties) and sediment grain size composition (μm) of sediment cores 1.1 and 8.2 by depth. Uncertainties are quoted at the 2 sigma level.

Site core	Depth (cm)	Total ^{210}Pb (Bq kg $^{-1}$)	Supported ^{210}Pb (Bq kg $^{-1}$)	Unsupported ^{210}Pb (Bq kg $^{-1}$)	^{137}Cs (Bq kg $^{-1}$)	CIC age (year)	CRS age (year)	Sedimentation (cm year $^{-1}$)	% Clay <2 μm	% Silt 2–20 μm	% Sand 20–200 μm	% Coarse sand 200–2000 μm
1.1	0–3	96	11 ± 1.8	85 ± 5.7	2.1 ± 0.4	9 ± 9	9 ± 3	0.2 ± 0.01	7	36	41	17
	3–6	65	11 ± 1.4	54 ± 3.6	2.2 ± 0.3	28 ± 9	27 ± 5	0.2 ± 0.01	6	30	55	10
	6–9	35	9 ± 1.2	26 ± 3.2	1.1 ± 0.2	46 ± 9	46 ± 7	0.2 ± 0.02	2.8	17	59	22
	9–12	23	7 ± 1.6	17 ± 1.9	0.6 ± 0.4	65 ± 10	64 ± 8	0.2 ± 0.03	3.5	15	44	38
	12–15	15	6 ± 1.4	9 ± 2.3	0.6 ± 0.2	83 ± 10	82 ± 9	0.2 ± 0.04	0.6	4	35	61
8.2	0–3	70	14 ± 1.8	56 ± 5.3	2.9 ± 0.4	4 ± 4	7 ± 2	0.4 ± 0.04	15	73	12	0
	3–6	64	16 ± 1.5	48 ± 5.3	2.7 ± 0.4	13 ± 5	11 ± 4	0.3 ± 0.03	15	74	11	0.2
	6–9	51	16 ± 1.5	35 ± 3.5	3.3 ± 0.3	23 ± 5	19 ± 5	0.3 ± 0.03	14	67	17	3.2
	9–12	38	16 ± 1.5	22 ± 5.2	2.6 ± 0.5	32 ± 6	25 ± 7	0.4 ± 0.07	15	68	11	6.3
	12–15	36	20 ± 1.4	16 ± 4.3	3.7 ± 0.4	41 ± 6.4	41 ± 6	0.3 ± 0.02	15	73	12	0.5

sedimentation rates of 0.2 and 0.3 cm year $^{-1}$ were found in site 1 (Griffins Bay) and site 8 (centre of the lake) respectively. The sedimentation rate found for site 1 is similar to that previously reported (Chenhall et al., 1994; Payne et al., 1997), but not for site 8 which had a rate reported as 0.9 cm year $^{-1}$ (Chenhall et al., 1994). This discrepancy can be explained by the different methodologies used. While this study uses ^{210}Pb , ^{137}Cs and metal profiles, Chenhall et al. (1994) only used sediment ash and metal profiles. There was a discrepancy between ash and metal concentration profiles in his study, with ash profiles resulting in a higher sedimentation rate.

Based on the results of this study, therefore, it is feasible to conclude that the sedimentation rate in Lake Illawarra from the 1930s have been constant at sites 1 and 8, indicating that human activity has not changed the sedimentation rate during this period.

4.4. History of anthropogenic metal contamination

The distributions of copper, zinc, arsenic, selenium, cadmium and lead concentrations within core 1.1 (Fig. 4) were in agreement with historical events in the southern part of the lake contributing to the inputs of metals. Contamination in the lake started below

core layers, which corresponds to the commencement of industrial activities in Port Kembla at around 1910–1920 and intensified in 1947, with the creation of a Greater City of Wollongong.

Core 8.2, however, showed a different metal concentration profile in sediments which does not match the history of contamination from Port Kembla industry or Tallawarra Power Station. The bottom layer of the core, which according to ^{210}Pb corresponds to the 1970s, should present an increase in metal concentrations, but a decrease of metal concentrations was found corresponding to the start of the power station. The decrease in metal concentrations expected in 1989 was only slight in core 8.2, with the greatest decrease in metal concentrations actually seen at the top of the core, corresponding to the years of 2006–2010. These results were not expected and make it difficult to propose a sensible explanation of historical changes in metal concentrations at this location. Even considering that sedimentation rates and dates may have been underestimated for this core and considering a sedimentation rate of 0.9 cm year $^{-1}$ as reported by Chenhall et al. (1994), changes in metal concentration profiles do not agree with historical inputs from Tallawarra Power Station or the Port Kembla Industrial Complex. The most plausible explanation for the anomaly in this core is that contamination is a result of the water flow movement spreading contaminants from Tallawarra Power Station, preventing them

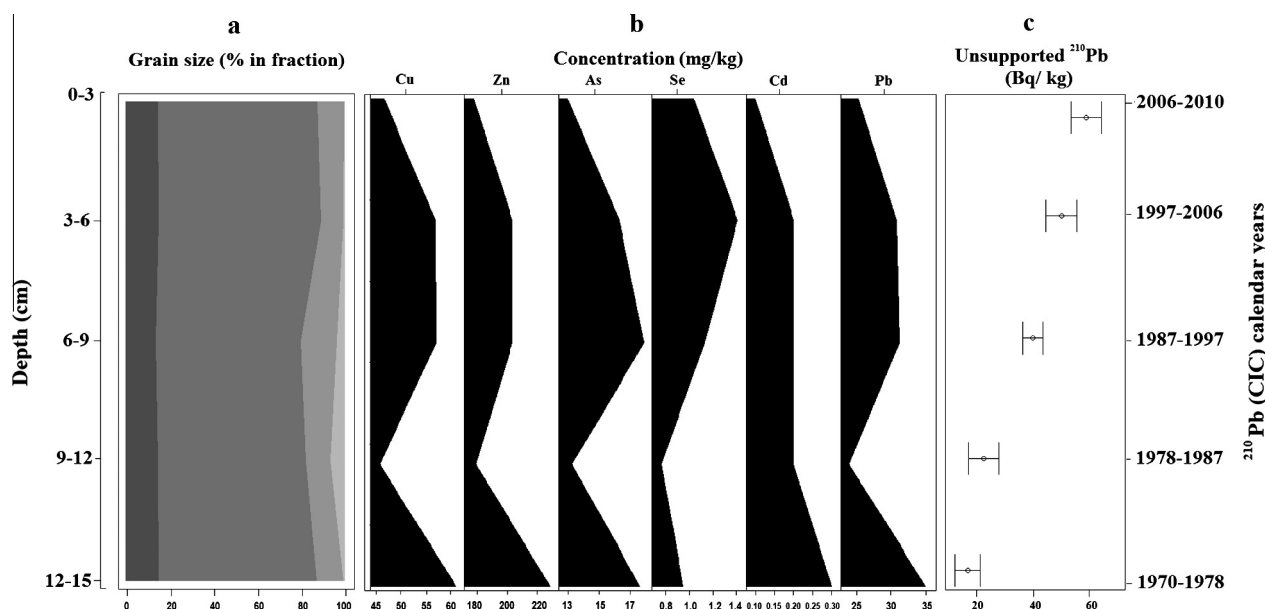


Fig. 5. Lake Illawarra (core 8.2) depth profiles of (a) grain size distributions with depth; dark grey % clay (<2 μm), medium grey % silt (2–20 μm), grey % fine sand (20–200 μm), light grey % coarse sand (200–2000 μm), (b) total metal concentration and (c) ²¹⁰Pb activity depth profile.

being concentrated in one spot (DECCW, 2009). In addition, the main source of metals according to history is the Windang Peninsula, an area located between the Pacific Ocean and the Lake. This region has been the subject of significant sand extraction activities, while granulated copper slag from a copper-smelter refinery in Port Kembla was dumped into the ground. Yassini (2004) reported this copper slag as consisting of aluminium, magnesium, zinc, copper, lead and cadmium. Although selenium concentrations were not reported by Yassini (2004), it is known to be produced from copper refinery slimes and from flue dusts from copper smelters (Hoffmann, 1989; Green, 2006). Examination of early aerial photography suggested that these activities may have begun as early as 1945 (Yassini, 2004), which agrees with the high concentration of metals in the base of the core corresponding to the period of 1970–1978.

4.5. Sediment metal concentrations and sediment quality guidelines

In Australia, the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ, 2000) outline the criteria for assessing site contamination and determining the requirements for further investigation, or assessment of risk to determine if any further action is required. This document advises further investigation if sediment metal concentrations are above the low trigger values of: Cd 1.5 mg kg⁻¹, Cu 65 mg kg⁻¹, Pb 50 mg kg⁻¹, Zn 500 mg kg⁻¹. There was no guideline established for selenium in Australia as a result of limited data availability.

In Lake Illawarra, the metal of highest concern is zinc, which was higher than the sediment quality guideline value at sites 1 and 8, and copper at sites 1 and 7, most likely as a result of Port Kembla industries rather than the activities of the Tallawarra Power Station.

5. Conclusions

Our results contribute to a body of evidence that Lake Illawarra has faced a history of metal contamination, manifested by their accumulation in deposited sediments. Metal concentrations peaked in the 1960s around the time that the Tallawarra Power

Station commenced operation, although elevated metal concentrations were present in the 1930s by which time a steelworks and copper smelter were in operation at Port Kembla. Our results for selenium and arsenic suggest that the coal-fired power station was not their main source to the Lake but the origin was Port Kembla. The metals of highest concern were zinc and copper, which exceeded the Australian sediment quality guideline values at sites 1 and 8 for zinc and sites 1 and 7 for copper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.06.058>.

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