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Trace Metals in sediments from Lake Illawarra, New South Wales, Australia

Bryan E. Chenhall
*University of Wollongong, bryanc@uow.edu.au*

Brian G. Jones
*University of Wollongong, briangj@uow.edu.au*

Craig R. Sloss
*University of Wollongong, csloss@uow.edu.au*

Mark O’Donnell
*University of Wollongong, mark_odonnell@uow.edu.au*

Marrack Payne
*University of Wollongong*

*See next page for additional authors*

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Authors
Bryan E. Chenhall, Brian G. Jones, Craig R. Sloss, Mark O'Donnell, Marrack Payne, Mark Murrie, David Garnett, and Helen Waldron

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ABSTRACT

Sediments in Lake Illawarra have been investigated by deep and shallow coring to provide a comprehensive appraisal of the sediment-bound natural (background) and more recent (i.e., industrial era) trace metal concentrations. The distribution of Cu, Pb and Zn in the upper 20 cm of sediment is directly related to the proportion of mud-dominated sediment forming the central floor of the lake. Trace metal enrichment factors for Cu, Pb and Zn were generally less than 2.5 with the exception of the southern portion of Griffins Bay where the factors were greater than 1.8, 3.5 and 5.8 for Cu, Pb and Zn respectively. According to ANZECC and ARMCANZ (2000) protocols, the sediments can be generally classified as low risk, although the sediments present in the southern part of Griffins Bay can exceed the high guideline value (ISQG-high) of 420 ppm for Zn and the low guideline values (ISQG-low) of 65 ppm and 50 ppm for Cu and Pb respectively. These sediments warrant further investigation in the form of ‘bioavailability’ and biotoxicity testing. Future work could be directed towards an assessment of the acid generation potential of these sediments due to the potential for pyrite oxidation facilitated by dredging and exposure to the atmosphere.

INTRODUCTION

Trace metal contamination of estuarine and lagoonal ecosystems is an inevitable consequence of rural, industrial and urban development and expansion. On a global scale, one key adverse environmental impact of trace metal contamination of the sediment (and water) column in aquatic ecosystems is the potential for transference of toxic (e.g., Pb, As, Hg) trace elements into the food chain (Wittman, 1981; Laliberte et al., 1992) which, in incidents of extreme exposure can result in mortality in humans.

Trace metal concentrations in estuarine and lagoonal sediments are a reflection of both natural (lithogenic) and anthropogenic sources which may be of point and non-point (diffuse) origin. As noted by Jones et al. (2003), natural (or background) concentrations are governed by factors including the lithology and surface processes operating in the catchment. Adequate knowledge of the contribution of background (baseline) trace metal concentrations to sediment loading is thus important in studies focussing on human impact in aquatic bodies.

The important role of estuarine and coastal lagoonal sediments as both a sink and a source for anthropogenic contaminants including trace metals has been widely recognised (Arakel, 1995; Kennish, 1997). Humans have
often regarded estuaries and open lagoonal systems as avenues for waste disposal under the misconception that discharged contaminants will be diluted and dispersed in adjacent open marine settings. However, as pointed out by Kennish (1997), in excess of 90% of the particulate matter (and its associated contaminants) arriving in estuaries and coastal lagoons settles out by flocculation (promoted by the transition from freshwater to saline conditions) with small amounts of this sediment reaching the open ocean. Bottom sediments thus can function as a sink for contaminants including trace metals but under changing environmental conditions (e.g., changing oxidation state, pH, bacterially-mediated processes) may also function as a dynamic medium for the release of these contaminants into overlying waters (Arakel, 1995; Jones et al., 2003).

This paper synthesises a number of research projects on the trace metal concentrations in Lake Illawarra sediments, and presents new geochemical data for a deep (8 m) vibracore collected from the centre of the lake.

LAKE ILLAWARRA

Lake Illawarra is a shallow (<3.5 m deep), almost landlocked, saline coastal lagoon located 80 km south of Sydney, near Wollongong, in New South Wales, Australia. The Lake originated circa 6500 years ago during the last Holocene high stand by the renewed growth of a Pleistocene coastal sand barrier (Windang Peninsula) across the eastern side of a shallow embayment and subsequent flooding of the captured river plain (Yassini and Jones, 1987). The physical and hydrological characteristics of Lake Illawarra have been documented in numerous studies (Eliot et al., 1976; Yassini and Jones, 1987; Payne et al., 1997). The microtidal (circa 3.3 cm) nature of the main body of the Lake (Eliot et al., 1976) and resultant restricted lake-ocean water exchange, together with periodic shoaling of the entrance result in effective sediment (and contaminant) retention except during periods of exceptionally high rainfall and flooding when suspended sediment is transported to the open ocean.

It has been estimated that in the period 1817-1993 approximately 47% and 20% of the catchment of Lake Illawarra was converted to agricultural and urban purposes, respectively, by removal of native vegetation. The Smelting Company of Australia (1896-1906) operated a custom base metal processing plant near Kanahooka Point. At present, the northern hinterland of the Lake is host to the diversified Port Kembla industrial complex, including Bluescope (BHP) Steel, a copper refining and smelting plant (closed in August 2003), coal and grain handling facilities, and chemical fertiliser works. Tallawarra Power Station, located on the western foreshore of the Lake commenced operations in 1954 was decommissioned in 1989 and demolished in the second half of the 1990s. Rapid urban expansion is occurring in the western and southwestern portions of the catchment; the Lake is now almost entirely ringed by urban and industrial development.

PREVIOUS AND CURRENT WORK

Trace metal concentrations of Lake Illawarra sediments have been the subject of a number of previous studies. The essential information
concerning these studies, together with methodologies utilised in the current study are summarised in Table 1. Further detail relating to sediment collection, preservation and analysis is presented in the papers referenced in column 4 of Table 1.

Sediment Distribution and Sediment Characteristics

Sand-dominated (i.e., >50% wt +63 µm fraction) sediments are distributed along the western foreshore of Lake Illawarra reflecting relatively high energy depositional environments of terrestrially-derived detritus associated with the prograding deltas of Mullet Creek, Duck Creek, Macquarie Rivulet and smaller creek systems including Brooks Creek. Significant sand deposits, representing marine-derived sand from the adjacent coastal barrier dune and beach systems, also occur along the Windang Peninsula and in the Lake entrance channel (Yassini and Jones, 1987). The percentage of sand rapidly declines as a function of distance, particularly from the western Lake foreshore with the central, deeper portions of the Lake being best described as a mud basin.

Sediments in the deeper portions of the Lake, thus, are characterised by in excess of 90% silt and clay-sized material (Yassini and Jones, 1987; Sloss et al., 2004).

Interstitial waters in Lake Illawarra sediments ranged in pH from 7.2 to 8.5 with 77% of the measurements constrained to the range 7.6-8.0 (Payne et al., 1997). A redox boundary is generally present in the upper 2-4 cm of sediment although the depth of this boundary is influenced by substrate type (i.e., slightly deeper in sandy sediments) and composition (Payne et al., 1997). The reduced nature of the sediments is consistent with the

Table 1. Previous and Current Studies of Trace Metals in Lake Illawarra Sediments

<table>
<thead>
<tr>
<th>Sample Acquisition</th>
<th>Method of Analysis</th>
<th>Metals Analysed</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 box cores 45-50 cm in length</td>
<td>AAS and Colorimetry of –150 µm sediment fraction</td>
<td>Cu, Pb, Zn, Ni and Co Mo and As</td>
<td>Roy and Peat (1974)</td>
</tr>
<tr>
<td>2 deep cores, 5 short cores, 13 dredge samples</td>
<td>AAS of –75 µm sediment fraction</td>
<td>Cu, Cd, Pb, Zn and Fe</td>
<td>Ellis and Kanamori (1977)</td>
</tr>
<tr>
<td>8 cores 60-100 cm in length</td>
<td>ICP MS XRF of bulk sediment</td>
<td>Cu, Pb, Zn, Mn, Cd, Fe*</td>
<td>Batley and Chenhall (1995)</td>
</tr>
<tr>
<td>40 cores 40-130 cm in length</td>
<td>XRF of bulk sediment</td>
<td>Cu, Pb, Zn</td>
<td>Payne et al., (1997)</td>
</tr>
<tr>
<td>8 m vibracore</td>
<td>XRF of -63µm sediment NAA of -63 µm sediment</td>
<td>Cu, Pb, Zn Cr, As**, Sb, Co*</td>
<td>This study</td>
</tr>
</tbody>
</table>

*other metals and elements (including REE, present study) analysed in these studies but not reported here
** the metalloid As is included
formation of diagenetic pyrite by bacterially-mediated sulfate reduction (Beveridge, 1987; Morse, 1994) with depth in the sediment column.

Anthropogenically-derived particulate matter (ash) has been identified in the near surface sediments (Yassini et al., 1995). Both siliceous carbonaceous ash particles can be recognised particles; such as pyrometallurgical (kish) graphite and siliceous (fly) ash are uniquely sourced to steelmaking and coal firing respectively (Chenhall et al., 1994).

**Background Trace Metal Concentrations**

Figure 1 presents the results of XRF analysis for a compaction corrected vibracore (7.8 m in length) collected from the central part of Lake Illawarra. Dating of the core was facilitated using amino acid racemisation (aspartic acid) techniques (Sloss et al., 2004; on Notospisula trigonella valves and records some 4000 years of sediment (> 90% mud) and trace metal accumulation in the central portion of the Lake. Concentrations of Cu, Pb and Zn display a remarkably uniform distribution with depth thus providing the basis for determination of background (‘pre-industrial’) values for these elements. Enrichment in Cu, Pb and Zn in the upper 50 cm of the core is equated with European (industrial) impact on the Lake. Sediments from the same intervals were analysed by neutron activation techniques yielding background

![Figure 1 Metal Distribution with depth in Central Core VC4](image)
concentrations for Sb, Cr, Co and the metalloid As. A summary of these data together with previous background concentration determinations is presented in Table 2.

Despite the different methods of sample pre-treatment and analysis (Table 1), the background concentrations of Cu and Pb are in very good agreement. Significant differences between the Zn background determinations of Ellis and Kanamori (1977), Payne et al. (1997) and the present study, could possibly be accounted for by analytical factors and the unusual grain size normalisation employed by Ellis and Kanamori (1977) which also includes a portion of the fine sand sediment fraction. However, a more feasible explanation is that the deep (10-20 m) sediments utilised by Ellis and Kanamori (1997) are in fact part of the geochemically distinct underlying Pleistocene succession. Small differences in background Zn concentration between the Payne et al., (1997) and present studies are probably attributable to sediment grain size factors and differences in sample preparation.

Chromium concentrations in pre-European sediments are most likely a reflection of the relative abundance of basaltic rocks (Dapto Latite),

Table 2. Background concentrations of elements (ppm unless stated) in Lake Illawarra and ANZECC & ARMCANZ (2000) Sediment Quality Guidelines (in mg/kg=ppm except for Fe in wt%)

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n=10</td>
<td>n=76</td>
<td>n=50</td>
<td>ISQG-low</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>5.9%(0.3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>20(2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>38</td>
<td>33(8)</td>
<td>37(7)</td>
<td>65</td>
</tr>
<tr>
<td>Zn</td>
<td>44</td>
<td>68(13)</td>
<td>84(11)</td>
<td>200</td>
</tr>
<tr>
<td>Pb</td>
<td>15</td>
<td>17(5)</td>
<td>18(4)</td>
<td>50</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>0.6(0.2)</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>76(4)</td>
<td>80</td>
<td>370</td>
</tr>
<tr>
<td>As</td>
<td>-</td>
<td>15(2.5)</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.1</td>
<td>-</td>
<td>1.5</td>
<td>10</td>
</tr>
</tbody>
</table>

1 calculated by ‘normalising’ to 100% of -75µm sediment fraction  
2 bulk sediment determination  
3 determined on sieved (<63µm) sediment  

n=number of samples used to determine background (mean) concentrations; standard deviation in brackets
volcanogenic sediments and their weathered equivalents around the lake periphery.

**Trace Metal-Sediment Grain Size Relationships**

A general relationship between increased trace element abundance in finer (<63 µm), organic-rich sediment has been widely recognised in aquatic environments (e.g., De Groot, 1995; Irvine & Birch, 1998). Data for Lake Illawarra are presented in Table 3.

These data are interpreted as follows. Positive, moderately strong correlations between Zn, Pb and Cu indicate that the trace elements may have a common, though not necessarily unique origin. Weak negative (but statistically significant) correlations between sand % and Cu and Pb indicate preferential concentration and retention of these elements in the finer mud fraction. Significant correlations between LOI% and Cu, Pb and Zn are suggestive of a relationship between these metals and organic matter. However, as pointed out by Leong and Tanner (1999) LOI is a poor proxy for organic carbon and thus trace metal-organic carbon relationships have not been clearly established for the Lake. The strong, negative correlation between Rb and sand% reflects the (illitic) clay content of the sediments and underpins the potential for use of ‘conservative’ elements such as naturally-occurring Rb as monitors of grain size-related variations in trace metal abundances.

**Anthropogenic Trace Metal Loading**

As indicated in Figure 1, trace metal contamination of Lake Illawarra sediments can be demonstrated by geochemical analysis of sequential slices of sediment cores and the construction of trace metal concentration-depth profiles (Ellis and Kanamori, 1977; Batley and Chenhall, 1995; Payne et al., 1997) which provide a comparison of the natural (background) and the near surface contaminated sediments.

**Contamination by Co, Cd, Cr, Sb and As**

Background concentrations for Cd have been established by previous studies and natural concentrations for Co, Cr, Sb and As were established in the present study (Table 1). Enrichment factors for the contaminated near surface sediment can be derived using the expression:

\[ EF = \frac{\text{conc. in the upper sediment fraction}}{\text{background concentration}} \]

An enrichment factor cannot be established for Cd since the

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**Table 3. Significant (99% confidence level) product moment correlations (r) for Lake Illawarra sediments (data source Payne et al., 1997)**

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Rb</th>
<th>Sand %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>*</td>
<td>0.72</td>
<td>0.73</td>
<td>0.36</td>
<td>-0.33</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>*</td>
<td>0.69</td>
<td>0.35</td>
<td>-0.30</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td>*</td>
<td>0.26</td>
<td>x</td>
</tr>
<tr>
<td>Rb</td>
<td></td>
<td></td>
<td></td>
<td>*</td>
<td>-0.90</td>
</tr>
</tbody>
</table>

x denotes not significant

Loss on ignition (LOI) \( r \) vs Cu, Pb and Zn are 0.69, 0.53 and 0.56 respectively
background concentration is below the detection limits of the measuring facilities. However, Cd concentrations in the upper sediment generally do not exceed 1 ppm. An exception to this pattern is present in the southern section of Griffins Bay where Cd concentrations range between 3-4 ppm (Ellis and Kanamori, 1977; Batley and Chenhall, 1995). Data for Co, Sb, Cr and the metalloid As are limited to the upper section of vibracore VC4 (Figure 1) from the centre of the Lake. All of these elements display slight enrichment above background, with EFs of 1.2, 1.7, 1.1 and 1.2 for Co, Sb, Cr and As respectively.

Cu, Pb and Zn

From an environmental standpoint, these metals are the most significant contaminants in Lake Illawarra sediments. Figure 2 illustrates the distribution of Pb and Zn as a function of depth in core LI6 (Chiaradia et al., 1997). Enrichment in Pb and Zn in the upper portion of the core is not related to fluctuations in grain size, since the Rb (an effective proxy for grain size) concentrations are uniform down core. The profile in Figure 2 is typical of most mud-dominated sediment cores from the central portion of the lake with both Zn and Pb showing significant enrichment in the upper 20-25 cm and a slight decline in concentration in the uppermost 5-10 cm of sediment. This decline in concentration is possibly equated with decreasing levels of sediment contamination as a consequence of more stringent industrial pollution control measures introduced in the 1970s. Trace metal contamination in this core extends down to 45 cm as evidenced by the systematic shift in 206/204Pb from natural values of 18.7 to values approaching 17.6 in the upper sediment (Chiaradia et al., 1997). The depths to which trace metal contamination extends in Lake Illawarra is site specific, possibly governed by the rate of sediment accretion as well as other factors such as sediment burrowing by benthic organisms and by geochemically-

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**Figure 2.** Rb, Zn and Pb distribution in LI6

![Figure 2](image-url)
mediated processes (Chenhall et al., 1995). Figure 3 depicts the general distribution of Cu, Pb and Zn in the near surface sediments of Lake Illawarra. The contour maps have been drawn using the mean trace metal concentration present in the upper 20 cm of sediment on the basis of the studies of Payne et al., (1997) and Chenhall et al., (1995). The maps illustrate the magnitude of relatively long term contamination of the sediment by trace metals. This sediment interval is most likely to be disturbed should dredging operations be contemplated and constitutes the zone of significant exposure risk to bottom-dwelling benthic organisms. All trace metals display a systematic distribution with respect to sediment grain size with the greater concentrations present in the muddy lagoonal sediments forming the floor of the central portion of the lake. Enrichment factors for Cu (Figure 3a), Pb (Figure 3b) and Zn (Figure 3c) in the mud-dominated sediments are generally <2.5. Concentration maxima of Cu (>60 ppm), Pb(> 60ppm) and Zn (>400 ppm) corresponding to enrichment factors of >1.8, >3.5 and >5.8 respectively are present in the southern portion of Griffins Bay.

DISCUSSION

Sources of Trace Metals in Lake Illawarra

Although trace metals derived from diverse sources, for example, Zn from galvanised iron, Pb from the combustion of petrol-Pb additives, and trace metals affiliated with domestic effluents (Wittman, 1981) probably contribute to trace metal loading in Lake Illawarra, a major source of trace metals is the Port Kembla industrial complex located near the north eastern margin of the Lake. The modes of delivery of trace metals to the Lake from industry are probably diverse and could include dispersal of industrially-derived trace metal-bearing ash (Payne et al., 1997) and the erosion, transportation and deposition by wind and water of contaminated soils near major industrial sites.

Ash uniquely sourced from steel manufacture, copper smelting and electric power generation is present in the Lake sediments (Chenhall et al., 1994) and a direct link between ash and dusts of industrial origin and metals including Cu, Pb, Zn and the metalloid As can be demonstrated (e.g., Chiaradia et al., 1997).

Sediment Quality

Lake Illawarra sediments are generally characterised by low (<2.5) enrichment factors for Cu, Pb and Zn and the current study together with previous work (Table 1) has tended to indicate that the maximum concentrations of these metals are present in the upper 20 cm of sediment. A notable exception is the sediment from southern Griffins Bay where higher enrichment factors characterise the sediment and probably reflect the proximity of this site to Port Kembla industry. These enrichment factors contrast strongly with data for more contaminated Australian east coast lakes. At the northern end of Lake Macquarie, the continuous operation of the Cockle Creek smelter has resulted in Zn and Pb contamination of up to 1-2 orders of magnitude greater than in Lake Illawarra (Roy & Crawford, 1984; Batley, 1987). The southern portion of Lake Macquarie exhibits a much lower degree of contamination, reflecting greater distance from the Cockle Creek Smelter point source. Trace metal data for Lake Illawarra
Figure 3a. Mean concentration of Cu in the upper 20 cm of sediment

Figure 3b. Mean concentration of Pb in the upper 20 cm of sediment

Figure 3c. Mean concentration of Zn in the upper 20 cm of sediment

Trace metals in sediments can be assessed against the ANZECC & ARMCANZ (2000) sediment quality guidelines (Table 2). This assessment indicates that the Lake sediments are generally classified as 'low risk'. However, sediment from southern Griffins Bay exceeds the high trigger value (ISQG-high) for Zn and the low trigger value (ISQG-low) for Pb and Cu. According to ANZECC & ARMCANZ protocols, these sediments should be subject to further investigation in the form of bioavailability assessment and possibly biotoxicity testing.

CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

Near surface (<50 cm deep) sediments in Lake Illawarra are contaminated with trace metals, the most environmentally important contaminants being Cu, Pb and Zn. Trace metal distribution is closely linked with sediment type, the greatest concentrations of Cu, Pb and Zn being concentrated in the fine grained mud-dominated sediments present in the central portions of the Lake. The sediments, in general, exhibit low trace metal enrichment and are classified as low risk according to ANZECC & ARMCANZ (2000) protocols.

Future research could be directed towards an assessment of trace metal bioavailability, particularly for the more contaminated sections of Griffins Bay, since little data exists for the relative ease with which trace metals can be mobilised from the sediments. The acid generation potential of the Lake sediments could also be investigated, particularly if future management options include dredging of portions of the Lake sediments.
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