THE REACTIVITY OF ANTHROPOGENIC LEAD IN THE MARINE ENVIRONMENT (RECREATIONAL FISHING AND FLUFFY LEAD)

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INTRODUCTION

Estuaries are areas of deposition for terrestrial and tide-influenced marine sediments. As the transition zone between land and ocean, estuaries are important environments in supporting a diversity of terrestrial and marine plants animals. Estuaries also act as important sinks for heavy metals and nutrients in the environment due to the unique physical and chemical nature of the water and sediments (Mota *et al*. 2004).

Lead (Pb) is a heavy metal that is extremely toxic to all living organisms under high concentrations and is one of the few toxic heavy metals that is deposited into the environment by humans with little concern for its ultimate fate. Lead occurs naturally in the Earth's upper crust at concentrations of 15 µg/g (Taylor & McLennan 1985) and the natural background level of lead in seawater is 0.03 µg/l (Jaworski 1978). Lead is found in its most valuable form in ore bodies as the sulfide, galena (PbS). It can be transported through environmental mediums via weathering of rocks and soils, emissions into the atmosphere from volcanoes, wind blown dust, sea spray, biogenic material and forest fires (Thornton *et al*. 2001). Lead accumulates easily in estuarine environments, occurring as either particulate or dissolved matter, and is believed to be reasonably inert in most natural waters with the result that small concentrations do not pose a major threat to the environment (Xintaras 1992, Scheuhammer *et al*. 1995, Kraepiel *et al*. 1997, Simpson *et al*. 2002, Mann *et al*. 1980). However, in urbanized or industrialized regions, atmospheric-sourced Pb from automobile emissions and smelting from mining, particulate forms of Pb sourced from effluent, Pb-based paint, mining operations and lost fishing sinkers have the potential—in large concentrations—to have a severe impact on the environment and to enter into the food chain (Chenhall *et al*. 2003). Ingestion of contaminated fish and shellfish by humans can lead to Pb poisoning.

STUDY SITE

This honours research project examined the distribution of Pb in the sediments of the Merimbula Lake, NSW. Merimbula Lake is a wave-dominated estuary, with high sediment trapping efficiency, naturally low turbidity, salt wedge/partially mixed circulation and a high risk of sedimentation. The fresh water flux enters the back lake through two small creeks: Boggy Creek in the north; and, Bald Hills Creek further south. Merimbula town centre is located to the north of the lake close to its outlet. The Princes Highway crosses the inlet by a 250 m causeway and a short bridge. A sewage treatment facility exists to the south of the lake and Merimbula airport runs parallel to the lake on the seaward side from the south of the lake to the bridge on the Highway. The inlet and causeway offer considerable resistance to tidal penetration. The closest major coastal industrial centre is over 300 km to the north in Wollongong. The estuary is used extensively for recreational and commercial fishing and for the cultivation of Sydney Rock Oysters (*Saccostrea Glomata*). Merimbula Lake estuary is also an important breeding ground for these oysters. During the peak tourist season in the summertime, populations in Merimbula swell significantly, increasing the environmental and ecological loading on the estuary. Based upon observations of local fishing hotspots within the estuary, and the number of times people fishing are required to replace Pb fishing sinkers after loss, estimates may be made as to an annual loss of sinkers in the estuary. This can be estimated against the basic premise that if only one fishing sinker is lost in a cubic metre of sediment, then the sediment will have 4 ppm higher Pb concentration.

OBJECTIVES

In estuarine systems, contaminants are often rapidly removed from the water via sorption processes. Given that Pb is reasonably inert in estuarine environments, it tends to accumulate in benthic sediments. However, Pb is not necessarily fixed permanently to sediments. Rather, it may be remobilised via chemical, physical and biological processes. Changes in environmental chemistry due to urban runoff, industry or recreational use may result in the mobilisation of a large store of Pb. This project aims to examine the conditions under which these processes will occur, therefore identifying how large scale Pb mobility and biological uptake of the toxic metal and its compounds can be prevented. This study will:

- Determine the concentrations of Pb in estuarine environments, with emphasis on the changing chemistry in a column of sediment with depth and its effects on metal mobility in the sediment. Particular attention will be paid to the input of Pb into the system in the form of Pb fishing sinkers;

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- Use sequential leaching techniques to determine a potential environment under which Pb will undergo mobilisation; and,
- Show the importance of understanding the mobility of Pb in estuarine environments for future pollution control and environmental stability.

METHODS

Four cores were obtained from the front and back lakes of the estuary (Figure 1a). Selected sediment samples were analyzed by X-Ray Fluorescence (XRF) and Laser Ablation Inductively-Coupled Plasma-Mass Spectrometry (LA-ICP-MS) to determine major and trace element concentrations, and by X-Ray Diffraction (XRD) to determine mineralogy. In addition to the bulk analysis, samples from one of the cores and a surface mud sample were analyzed by a sequential extraction procedure to determine how Pb is portioned in the different sediment phases. Sequential leaching of a sediment sample provides comparative information of trace metal mobility in dynamic environmental conditions, such as those dictated by changing conditions such as pH or redox potential. Parameters such as pH, cation exchange capacity, particle size distribution, organic carbon and carbonate content and total sulfur affect the mobility of heavy metals.

The BCR (now the Measurements and Testing Programme of the European Commission) sequential extraction protocol is a standard procedure for the characterization of heavy metals in soils and sediments (Ho *et al.* 1997). The method used in this project is a modified version of the optimized BCR sequence (Sutherland *et al*. 2003). The selective sequential extractions were done on wet samples so as to obtain a result closest to that seen in nature. Duplicates of each sample were used in order to assess the error.

The extraction solutions were:

1. Water extractable (elements that are exchangeable and easily soluble salts);
2. Acid extractable (elements that are bound to the carbonate phase);
3. Reducible (elements that are bound to Fe-Mn oxides);
4. Oxidizable (elements that are bound to organic matter); and,
5. Residual metal phase (elements that are bound to any remaining components of the sediment).

Supernatant solutions were filtered and analyzed for major and trace elements by ICP-Atomic Emission Spectrometry (-AES) and ICP-Mass Spectrometry (-MS). Individual Pb sinkers were placed in a known location (location 1, after sediment was cored) in the front lake of the estuary for a period of 4 months. The Pb sinkers were brand new (with no corrosion salts present on them) at the time of deposition into the sediment. Fishing sinkers that were sourced from the beach, submerged in the estuarine sediment, and suspended in the water column were analysed by XRD and Scanning Electron Microscopy (SEM) using the attached Energy-Dispersive X-Ray Spectrometer (EDS) system.

RESULTS AND DISCUSSION

Sediments

The sediment cores were analysed for trends in major and trace element abundances and mineralogy. The results of the bulk analyses of the cores taken from Merimbula show Pb concentrations ranging between 2.8 ppm (core 3, 17 cm depth) and 21.4 ppm (core 1, 3 cm depth) (Figure 1b). The majority of the analyses fall between 8 and 12 ppm the Pb concentration is variable with depth and with location in the estuary. In core 1, which was taken from a location where sinkers are frequently lost, Pb concentration is highest in the surface sample and then is relatively constant at ca. 10 ppm with depth. Core 2 shows the opposite behaviour, in the upper ca. 50 cm Pb is relatively constant at ca. 10 ppm and then increases with depth. Core 3 and 4 have relatively constant Pb concentration with depth, although core 3 from the back lake, has lower Pb concentrations than the other three cores. An organic-rich anoxic mud sample collected from surface sediments from the back lake had the lowest Pb content at ca. 3 ppm. An anthropogenic Pb input can clearly be seen in the comparison of front lake and back lake bulk chemistry (Figure 1b).

Different sites sampled showed distinctive trends in metal concentration variation. Cores sampled from the front lake had a much higher trace metal loading, whilst sediments from the back lake had lower concentrations. Since the mud sample collected from the back lake was richest in organic matter, it was an ideal site for metal binding. Although this sample had the most Pb extracted from it, this sample contained the least total Pb. This indicates the importance of binding sites in sedimentary phases. Selective sequential extractions determined that Pb was strongly bound to the Fe and Mn-rich phases in the sediment and could only be extracted through a strong acid/aqua regia digestion. These results support previous work outlining the geochemistry of particulate and dissolved Pb in aqueous solutions.

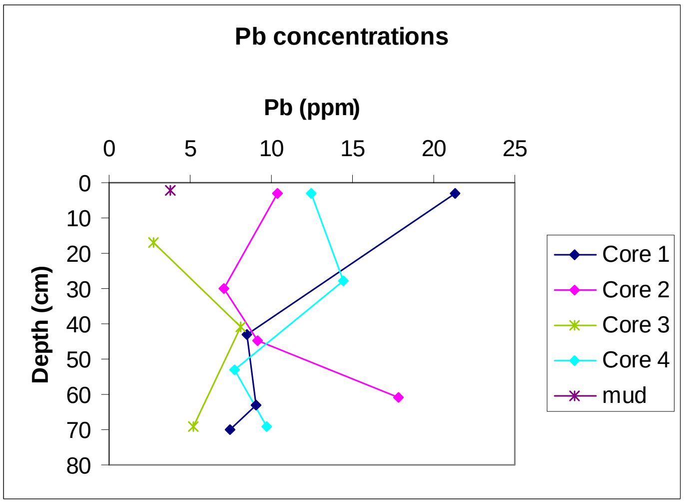

Figure 1a (top): Oblique aerial photograph of Merimbula lake with sampling locations Photo: Department of Land and Water Conservation, NSW.

Figure 1b (left): Cores 1, 2 and 4 are marked by diamonds and are sourced from the front lake; core 3 and the mud are marked with a star and are sourced from the back lake.

Sinkers

Four sinkers were analysed for alteration products on their surfaces. The corrosion products on the Pb fishing sinkers were analysed by XRD and SEM to determine the major mineral phases present. SEM and EDS showed significant differences between the compositions of the alteration products of the three fishing sinkers sourced from: 1) the beach for an unknown period of time; 2) buried in submerged sediment for a fixed period of four months; and, 3) suspended in the water column for a fixed period of four months, in comparison to; 4) a fresh sinker.

The fishing sinkers that were buried in submerged sediment and suspended in the water column for a period of four months were covered in a white residue when retrieved. SEM analysis showed the surfaces were highly altered (Figures 2, 3 and 4). The crystallography of these mineral phases was both platy in structure, as well as having a 'fluffy' appearance. The composition of the secondary phases is predominantly Pb chloride, Pb carbonate and Pb oxides. The alteration products varied between the sinkers as follows:

1. The fishing sinker retrieved from the beach (Figure 2) was predominantly composed of Pb, and its corrosion products Pb hydroxide, Pb chloride, cerrusite and Sn oxide, with trace amounts of phosgenite, quartz, Na phosphate, portandite and Co oxide. SEM imagery showed a $PbCO_3$-$CaCO_3$ solid solution, defined by zonation chemistry. The image shows Pb-rich carbonate (cerrusite; lighter areas) coexisting with Ca-rich carbonate (dark areas). The coexistence of two distinct carbonates is consistent with the presence of a solvus in the Ca-Pb system (Chang & Brice 1972). This provides

evidence for the reaction of Pb with seawater. The Pb minerals had a “fluffy” appearance.

2. The buried fishing sinker (Figure 3) showed well-formed crystals of Pb carbonate, Pb chloride, Pb oxides, halite and quartz. XRD analysis determined minerals to be phosgenite, cerrusite, Pb, Pb oxide, anglesite, malayaite and Pb carbon hydrogen oxide.

3. Gouge marks on the suspended sinker (Figure 4) lacked flaky alteration minerals over most of the surface unlike the other two sinkers from the same environment. Sparse patches of clays were present on the surface (alumino-silicates). The bulk of the surface appeared to be relatively unaltered. However, there was biological material and some crystalline and ‘fluffy’ material adjacent to a seam on the sinker, which could act as a barrier, suggesting the surface had been extensively altered and that the delicate alteration products had been scoured away from the rest of the surface.

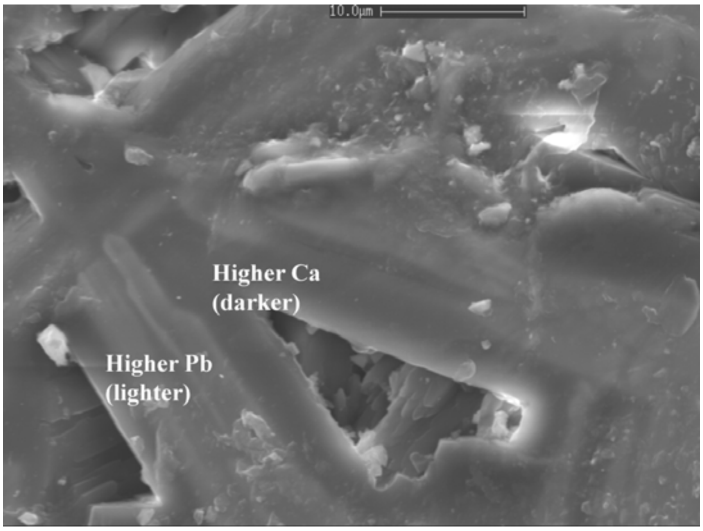

Figure 2: SEM image of the surface of a sinker sourced from the beach, showing coexisting Pb-rich- and Ca-rich carbonate.

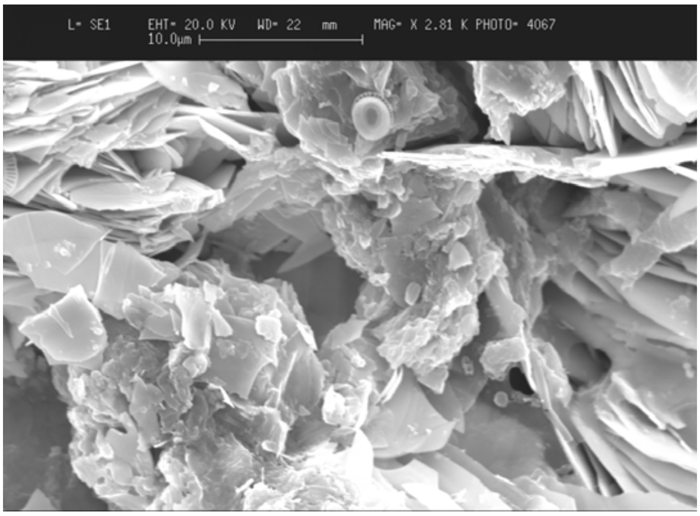

Figure 3: SEM image of the surface of the submerged fishing sinker. Well formed crystals of Pb-carbonates, -chlorides and -oxides are present.

The major species present on the surface of the fishing sinkers were Pb chlorides, Pb carbonates and Pb oxides. These are relatively insoluble in water. Rough estimates of the Pb flux from the sinkers into the estuarine sediments can be determined based upon the results of the sediment cores and the fishing sinkers. In the case of solid metal Pb fishing sinkers, the flux of Pb from the sinkers into the sediments can be estimated. The formation of Pb salts on the surface of the sinkers is a result of Pb metal being unstable under normal surface conditions. Lead salts form on the surface to protect the metal from further corrosion. In seawater, where carbonate and chloride anions are in abundance, this complexation process occurs easily. Physical processes occurring at the sediment-water interface, such as wave and tidal movement and biological activity, cause disturbance of the sediment, the gradual removal of the alteration products on the surface of the sinkers and mobilization of these salts into the water column and sediment. Sinkers that become buried in the sediment, where conditions are protected, are less likely to disperse Pb into the sediment. Bioturbation, however, may be a complicating factor.

Although Pb entering an estuary, whether in particulate, solid or molecular form, will eventually become incorporated into the sediment, many factors will vary the pathways to this final ‘resting’ point. This will impact on the potential for which these Pb species are bioavailable before settling into the sediment.

CONCLUSIONS

Data from the sediments provide evidence for an increase in Pb in different parts of the lake, however, the source of the contamination (whether from Pb sinkers, or other anthropogenic activity) is unknown. SEM analysis showed the sinkers could become highly altered over a short time period, with removal of the alteration product being dependent on the physical environment. It is unclear how rapidly material will be dispersed. Variations in geochemical environments, such as between the core and mud samples, indicated large variations in Pb concentrations. These results indicate the importance of the depositional environment in the ultimate concentrations of Pb in estuaries. In both the short and the long term, Pb fishing sinkers do not present a risk to estuarine habitats if left undisturbed. In the case of Merimbula Lake, where acid sulfate soils are not a problem, even dredging will not cause Pb to be remobilized due to the carbonate present in seawater acting as a buffer to dramatic pH changes. In regions where excessive contamination of potentially reducing agents occurs, such as sulfides, the risk of soils becoming more acidic is increased, and stores of Pb in the sediment in both molecular or particulate form could be at risk of becoming remobilized and therefore bioavailable.

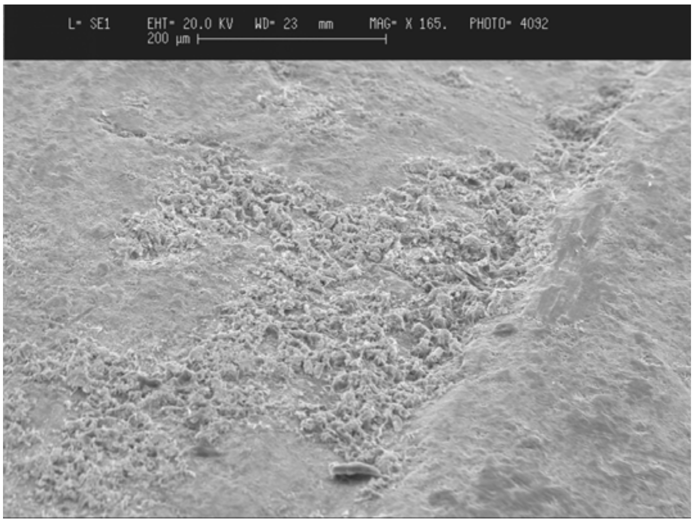

Figure 4: SEM image of the surface of the sinker suspended in the water column. The surface of the sinker has a “bald” appearance in comparison to others.

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