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supervising scientist report





MOUNT LYELL REMEDIATION

The behaviour of copper in sediments and waters of Macquarie Harbour, western Tasmania

Peter Teasdale, Simon Apte, Graeme Batley & Phillip Ford

Mount Lyell Remediation Research and Demonstration Program

a Tasmanian and Commonwealth Government initiative

supervising scientist report

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A joint program between the Supervising Scientist and the Department of Environment and Land Management, Tasmania.

This report describes research that is part of the Mt Lyell Remediation Research and Demonstration Program, a joint program between the Supervising Scientist and the Department of Environment and Land Management, Tasmania.

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Executive summary

The Mount Lyell copper mine in Queenstown, western Tasmania, has discharged tailings and waste water into the King River from 1916 to 1994. Over this period it has been estimated that in excess of 100 million cubic metres of tailings, slag and topsoil were deposited in the King River and Macquarie Harbour. As a consequence of this activity, high copper concentrations have been measured in the King River and Macquarie Harbour. This waste material has accumulated along the banks of the King River and has formed a large, unstable delta where the river enters the harbour. Exposed tailings material, both on the delta and on the river banks, is highly acidic as a result of pyrite oxidation and this contributes to the dissolution of both iron and copper from these sediments.

The Mount Lyell Remediation Research and Demonstration Program is undertaking a comprehensive study of the impacts of the Mount Lyell mine operation on the King River and Macquarie Harbour as part of the development of a remediation strategy. This report describes a comprehensive study of the cycling of copper in the sediments and waters of Macquarie Harbour, undertaken as project 12 within this program. The specific objectives of this project were to characterise the potential for sediment in Macquarie Harbour to release metals to the water column, to determine the conditions under which this will occur and to estimate the magnitude of increase of metals in the water column. Any options for reducing the release of metals from the sediment were also to be canvassed.

Field trips to Macquarie Harbour were in June and July 1995. Ten study sites of primary interest were selected, including three sites in the vicinity of the King River delta, one site in the entrance to Long Bay, five sites spaced approximately equidistantly along the east coast of the harbour, between the mouths to the King and Gordon Rivers, and a western harbour site. Water and sediment core samples were taken at each site and analysed for a range of chemical parameters. Pore water samplers (peepers) were used to obtain information on the pore water copper concentrations. Sediment traps were used at selected sites in the harbour in order to determine the sedimentation fluxes of particulate material.

Dissolved copper concentrations were determined largely by the mixing of river water and seawater and precipitation of river-borne copper in the low salinity zone of the estuary.Elevated concentrations of dissolved copper were measured throughout Macquarie Harbour. The highest dissolved copper concentrations were measured in the delta waters (up to 560 μ g/L). Elsewhere, surface water copper concentrations ranged from about 100 μ g/L in the north to 12 μ g/L in the south. Bottom water concentrations ranged from about 30 μ g/L on the delta to 4 μ g/L in the south. About 65--85% of the copper at all sites was in the filterable fraction (<0.45 μ m) and was probably present in the form of small particles (colloids) in association with iron and manganese. The copper complexation capacity of dissolved organic matter was exceeded in most harbour waters and a significant proportion of the dissolved copper may therefore be bioavailable.

Particulate copper concentrations in harbour sediments from all except the southernmost sites exceeded sediment quality guideline criteria formulated overseas, reaching over 1300 mg/kg at some sites. High particulate copper concentrations result from the deposition of copperladen tailings material in the northern harbour and the precipitation of colloidally-associated copper in the southern harbour. Copper was effectively immobilised in the southern harbour sediments by the presence of high levels of reactive sulfide which forms insoluble precipitates with copper. Acid-volatile sulfide measurements predicted low sediment toxicity at the southern harbour sites, whereas the toxicity of sediments from the northern harbour sites were predicted to be potentially high as a consequence of the low sulfide levels.

Pore water copper concentrations measured on the delta were as high as 4000 μ g/L in locations that experienced recent sediment deposition or disturbance. This has serious implications for proposed dredging of the tailings material. At the more stable regions of the delta, and for the rest of the northern harbour region where tailings material had been deposited, pore water copper concentrations were in the order of 50–500 μ g/L. Based on the pore water copper profiles, a flux of about 35 700 kg/y of dissolved copper from the sediment to the overlying water was calculated for the delta region. The pore water copper concentrations in the south were less than 8 μ g/L at the surface sediments and decreased to less than 2 μ g/L at depth. The low copper concentrations are a result of high sulfide concentrations which control the solubility of copper in the sediments and maintain a flux of dissolved copper from the water column into the sediment.

Fluxes of copper in sedimenting particles, which also act to remove copper from the water column, were calculated to be 46 000 kg/y on the delta. This is slightly greater than the flux of dissolved copper out of the sediments, thereby making the delta a net sink of copper under the conditions experienced during this study. The flux of particulate copper from the water column into the sediment for the rest of the harbour was about 85 000 kg/y. A mass balance calculation indicated that copper inputs for the King River were at least 95 000 kg/y, making it the source of 75% of the copper into the harbour waters. It must be stressed that the mass balance calculations presented in this work represent only a snapshot of the system and do not take into account temporal variations in copper transport or cycling.

A preliminary conceptual model of copper cycling in Macquarie Harbour has been proposed. Based on the nature of the sediment and the measured copper fluxes, there are three distinct zones. In the King River delta zone there are significant fluxes of dissolved copper from the sediments to the water column. The 'northern' harbour zone is characterised by a lower flux of copper but is a geographically larger area. The 'southern' harbour zone however, acts as a sink for dissolved copper as a consequence of the sulfide-rich surface sediments.

Based on this study, it is clear that there is a substantial input of dissolved copper to the Macquaric Harbour from the delta sediments. This will remain a potential problem even after the major source of copper to the system, the King River, has been remediated. The pore water chemistry studies suggest that there is likely to be remobilisation of dissolved copper during dredging operations. Further studies are required to assess the magnitude of this problem. Increasing the sulfide and organic matter concentrations of the sediments, possibly through revegetation, is likely to reduce the flux of copper from the delta.

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1 Introduction

The Mount Lyell copper mine in Queenstown, western Tasmania, has discharged tailings and waste water into the King River from 1916 to 1994. Over this period it has been estimated that in excess of 100 million cubic metres of tailings, slag and topsoil was deposited in the King River and Macquarie Harbour. As a consequence of this activity, high copper concentrations have been measured in the King River and Macquarie Harbour. This waste material has accumulated along the banks of the King River and has formed a large, unstable delta where the river enters the harbour. The path of the river to the harbour frequently alters with changes in river flow.

Exposed tailings material, both on the delta and on the river banks, is highly acidic as a result of pyrite oxidation and this contributes to the dissolution of both iron and copper from these sediments. Consequently, there is still a substantial load of copper that enters Macquarie Harbour despite discharge from the mine site having ceased. Previous studies by the Tasmanian Department of Environment and Land Management (DELM) have shown that the accumulation of copper-rich sediments has occurred virtually throughout the harbour, although it is greatest in the delta region extending in parts to well over a metre in depth. Of particular concern has been the long term fate of copper in the harbour, the fluxes of copper to and from the sediments and the impact that chemical and physical processes in the sediment may have on the ultimate bioavailability of copper.

The Mount Lyell Remediation, Research and Demonstration Program is undertaking a comprehensive study of all aspects of the impacts of the operation of the Mount Lyell mine and smelter on the King River and Macquarie Harbour as part of the development of a remediation strategy. This is a report on Project 12 within this program, which comprises a detailed study of the cycling of copper in the sediments and waters of Macquarie Harbour. The report also reviews the behaviour of copper in estuarine systems and evaluates previous studies of the region.

By its nature, this project needed to consider not only the sediments, but also the behaviour of copper in the water column, as these are closely related. The study is closely linked to other projects within the program which, model the behaviour of copper in the water column, studying the toxicity of harbour waters to aquatic biota and the behaviour of tailings in the King River.

The specific objectives of this project were to characterise the potential for sediment in Macquarie Harbour to release metals to the water column, to determine the conditions under which this will occur and to estimate the magnitude of the impact on the level of metals in the water column. Any options for reducing the potential impact on the release of metals from the sediment were also to be canvassed.

2 Behaviour of copper in estuarine systems

2.1 Introduction

In natural waters, the environmental chemistry of copper is dominated by changes in pH, salinity and redox potential (Eh). The dissolution of particulate copper and the precipitation of dissolved copper will be controlled by complexation and adsorption. Collectively these processes lead to partitioning of copper between overlying waters and sediments, which will influence the bioavailability and ultimate impacts of copper in both phases. The current state

of knowledge of these processes are reviewed in the following sections of this report. Also discussed are some of the findings of previous investigations and the tools that are proposed to be employed in this study to further assess the fate of copper in the sediments and water of Macquarie Harbour.

2.2 Fate of copper during estuarine mixing

2.2.1 Mixing processes

The mixing of riverwater and seawater results in strong chemical concentration gradients. Apart from dilution, a number of chemical reactions may also occur. The most important reactions, in terms of fate and transport of contaminants such as copper, are those which lead to a transfer or partitioning between dissolved and particulate phases. Chemical constituents that do not undergo significant reactions during estuarine mixing, such that their overall concentrations can be explained by the dilution of riverwater with seawater alone, are termed conservative constituents. These include most of the major ion constituents of seawater and riverwater such as sodium, magnesium, calcium, chloride, bicarbonate, nitrate and sulfate. As a result of the conservative behaviour of most major ions, salinity is also a conservative parameter. Constituents that undergo a significant reaction, which results in either an increase or decrease in their concentration compared to that expected by theoretical dilution alone, are termed non-conservative constituents.

The reactivity of dissolved chemical constituents in estuaries is usually assessed by plotting their concentration against a known index of conservative dilution such as salinity, although chloride concentration (expressed as chlorinity) is also commonly used. Conservative constituents exhibit a linear relationship with salinity, whereas constituents that undergo a chemical reaction in the estuary have curved salinity-concentration plots. A concave curvature is indicative of removal from solution (eg a precipitation or adsorption reaction) whereas a convex profile indicates inputs into solution (eg dissolution or release from sediments). Some idealised salinity-concentration plots are shown in figure 2.1. In some cases, both release and removal processes may occur giving rise to complex mixing profiles:



Conservative index of mixing

Figure 2.1 Idealised dilution behaviour of dissolved chemical constituents in an estuary (a) component concentration greater in seawater than riverwater (b) component concentration greater in riverwater than seawater ----- non-conservative behaviour; ----- conservative behaviour

The most important mechanism that results in non-conservative behaviour of chemical constituents is the floculation of colloidal material in the 0–5‰ salinity region. Virtually all aquatic particles carry a net negative charge in natural waters as a result of surface coatings of natural organic matter (Hunter & Liss 1979, 1982). These coatings form rapidly, as soon as particles are introduced into natural waters, and it has been shown that, in riverwaters, they play an important role in determining the stability and coagulation properties of natural particles (Gibbs 1983). With the sudden change in solution ionic strength that occurs in the low salinity region of an estuary, the overall net negative charge on the particles and colloids is reduced, resulting in aggregation and the formation of stable flocs. The coagulation of particulate material less than 0.45 μ m filter, will result in non-conservative behaviour (Morris & Bale 1981, Sholkovitz 1976, 1978, Fox & Wofsy 1983).

Iron, in particular, is markedly affected by the estuarine flocculation process. Under the oxidising conditions normally encountered in rivers, the predominant oxidation state is iron(III). Iron(III) has a very low solubility in riverwater, however observed iron concentrations are much higher in riverwaters than predicted by theoretical calculations. This is due to the formation of iron colloids which are stabilised by coatings of natural organic matter (NOM). The estuarine flocculation process results in the removal of a large proportion of colloidal iron (Fox 1983, Mantoura & Woodward 1983, Moore et al 1979). Field evidence suggests that iron removal is a fairly universal process occurring in most estuaries throughout the world (Morris & Bale 1981, Boyle & Edmond 1977, Moore et. al 1979). The majority of riverine humic acids are also removed during estuarine flocculation. The mechanism for this removal is either co-flocculation with colloidal iron (a large proportion of humic acids may actually be associated with the iron colloids), adsorption onto larger particles or direct precipitation from solution. It is highly likely that any trace metals bound to this humic material will also be removed from the dissolved phase. Although complete removal of riverine humic acids during estuarine mixing has been observed in some estuaries (Mantoura & Woodward 1983), dissolved organic carbon (DOC) is a conservative constituent. This is because riverine humic acids typically comprise less than 10% of total DOC (Mantoura & Woodward 1983, Fox 1983, Moore et al 1979).

It is important to appreciate that the formation of larger particles (>0.45 μ m diameter) through the coagulation of colloids does not necessarily imply that this material will settle from solution, especially in turbulent waters. It does point however, to a change in the physico-chemical form of the chemical constituent. Indeed, in most estuaries it appears that *total iron* (particulate plus dissolved) behaves conservatively whereas dissolved iron is highly non-conservative (Mayer 1982, Hong & Kester 1985). There is also little evidence to suggest that accumulation of iron and other trace metals in benthic sediments occurs in the low salinity region of estuaries.

The colloidal flocculation processes can also remove dissolved trace metals from solution either by coprecipitation during the coagulation process or by adsorption onto the surfaces of newly formed flocs. Copper in particular, has a high affinity for iron hydroxides (Ballistrieri & Murray 1982) and the potential removal of copper from solution in estuaries has been demonstrated in a number of laboratory modelling studies (Sholkovitz 1978, Sholkovitz & Copeland 1981, Millward & Moore 1982).

2.2.2 Adsorption/desorption behaviour

Adsorption of trace metals onto particulate material is a process of critical importance affecting trace metal distributions in natural waters. Currently, it is believed that there are three components of natural particles that are responsible for the majority of trace metal sorption reactions (Lion et al 1982, Tessier 1992). These are iron hydroxides, manganese hydroxides and natural organic matter. Surprisingly, aluminosilicates, which are a major constituent of most natural particulates, are not believed to play an important role in either freshwater or marine environments (Tessier 1992, Davies-Colley et al 1984). Their role is as a physical support for surface coatings of the sorbing phases.

The zone of maximum turbidity, turbidity maximum, occurring in the low salinity zone of many estuaries, has been demonstrated to be an important region for the adsorptive removal of trace metals (Morris & Bale 1981). Morris (1986) demonstrated that, in the Tamar estuary (UK), riverborne trace metals, including copper, are rapidly scavenged from solution by suspended particulate material located in the turbidity maximum. The continual resuspension and sedimentation of particles within this region maintained a supply of fresh sediment with high adsorptive affinity for trace metals.

Above salinities of ca 10‰ adsorption of trace metals onto suspended particulates is rarely observed on a scale that can be detected using salinity/concentration plots. This is because particle concentrations are generally low and the concentrations of divalent cations (eg calcium and magnesium), which can compete with trace metals for sorptive sites on particles, are extremely high. Significant adsorptive processes seem to be confined to the low salinity regions of an estuary, particularly within the turbidity maximum, where solids concentrations are greatly elevated (Morris 1986).

Desorption of trace metals from riverine particles may also occur in the low salinity zone, principally as a result of competition for binding sites from divalent cations such as magnesium and calcium. Desorption processes are often overshadowed by the competing processes of flocculation (see above) and adsorption (Bourg 1987) which also occur in the same region.

For some metals, the formation of soluble chloro-complexes is a factor controlling desorption from riverine particulates. This process has been shown to be important for cadmium in estuaries (Comans & Van Dijk 1988). Once again, this process occurs in the low salinity zone of estuaries where there is a steep gradient of chloride concentration. The effects of chloride complexation on copper, however, are negligible owing to the low affinity of copper for the chloride ion in saline solutions.

2.2.3 Effect of pH

Changes in pH can affect sorption processes (eg Salomons 1980, Fuller & Davis 1989) and the speciation of many metals in solution. The pH of riverwater is typically 7.0–8.0, whereas seawater has a well buffered pH of around 8.2. In the majority of estuaries there is, at most, a ten-fold decrease in hydrogen ion concentration from river to sea, though in the Macquarie Harbour the change will be considerably larger because of the low pH of the King River. Generally speaking, pH changes of this magnitude are not great enough to cause major changes in metal sorption unless the reactions are particularly pH sensitive. The adsorption reactions of copper onto estuarine sedimentary phases have been shown to be unaffected by pH changes over this range (Davies-Colley et al 1984). In reality, the orders of magnitude changes in the concentration of suspended sediments and of dissolved ions such as magnesium and chloride that occur over the estuarine salinity gradient, are likely to exert a much greater effect.

2.2.4 Solution speciation and complexation by natural organic matter

The bioavailability and toxicity of copper is critically dependent on its chemical speciation. Inorganic copper species, particularly the free metal ion, are the most toxic and bioavailable, whereas copper complexes formed with natural organic ligands are regarded as being essentially non-toxic. The extent of copper complexation by natural organic matter (NOM), and the capacity of the water to complex additional metals are important factors in natural waters. When copper complexing capacities are exceeded, a greater proportion of copper will be present in a more bioavailable form and impacts of copper on aquatic biota may result.

It is now well established that the solution speciation of copper, in virtually all natural waters, is dominated by complexation with natural organic matter. In river waters, greater than 99% of dissolved copper is believed to be present in the form of copper-NOM complexes (Mantoura et al 1978). Originally, it was thought that organic complexation in saline waters was less important owing to the competition for binding sites afforded by calcium and magnesium ions, which are present in these waters at much higher concentrations. In fact, it was believed that river-borne organic copper complexes would be rapidly dissociated in estuaries owing to this competition (Mantoura et al 1978). A growing body of information accumulated over the last ten years has, however, indicated that copper speciation in marine waters is also dominated by complexation with natural organic matter (Duinker & Kramer 1977, Van den Berg 1984, Van den Berg et al 1987, Coale & Bruland 1988, Apte et al 1990). Even in seawater, inorganic copper species represent only a very small fraction of the total metal (typically <1%). Copper complexation capacities in marine waters are usually in excess of total copper concentrations indicating a capacity to complex added copper.

There have only been a few studies of copper speciation in estuarics (Van den Berg et al 1986a, 1986b and 1987, Apte et al 1990) but these convincingly demonstrate extensive copper complexation by natural organic ligands. Maximum and minimum copper complexation capacities observed in estuaries are summarised in table 2.1. In all cases reported to date, copper complexation capacities are in excess of dissolved copper concentrations. The lowest values are found in the most saline waters, where dissolved copper copper concentrations are also the lowest. The copper complexation capacity of the surface waters of the Northeast Pacific Ocean is typically 0.6 μ g/L whereas dissolved copper concentrations are less than 0.05 μ g/L (Coale & Bruland 1988).

In a recent study of copper speciation in the Severn estuary (UK) (Apte et al 1990), it was shown that both dissolved copper and copper complexing ligands behave conservatively during estuarine mixing (figure 2.2) and as a result, copper is transported to the occans in the form of stable organic complexes. The main source of the copper-binding ligands is the river. The natural organic ligands have a strong affinity for copper and form complexes with estimated log conditional stability constants (log K) of between 11.4–12.8 (the higher this value, the greater the binding of copper to the NOM ligands will be). These values are greater than the conditional stability constant for the binding of copper in seawater by the synthetic chelator ethylenediaminetetraacetic acid (EDTA). Conditional stability constant data for metal complexes and natural organic ligand complexes should, however, be treated with caution. Because of the limitations of analytical techniques employed to measure these constants, most values are likely to be underestimates.

| Estuary | Copper complexation capacity (µg/L) | | Reference |
|-----------------------|--|---------|----------------------------------|
| | Maximum | Minimum | |
| Severn, UK | 12.5 | 0.9 | Apte et al 1990 |
| Gt Ouse, UK | 32.7 | 6.8 | Gardner and Ravenscroft 1991a, b |
| Tweed, UK | 24.3 | 2.5 | Gardner and Ravenscroft 1991b |
| Scheldt, Holland | 13.1 | 1.8 | Van den Berg et al 1987 |
| Guanabara Bay, Brazil | 19.1 | 2.5 | Van den Berg et al 1986b |

Table 2.1 Copper complexation capacities in estuarine waters



Figure 2.2 Effect of salinity on copper complexing capacity in the Severn estuary, UK (Apte et al 1990)

As noted earlier, copper has a high adsorptive affinity for hydrous iron oxides and as a result co-removal with iron in the low salinity region of estuaries may well be expected. The findings of recently published studies on the estuarine behaviour of copper around the world (table 2.2) illustrate the variable nature of copper behaviour. Both conservative and non-conservative behaviours (including both release and removal) have been observed.

The variability of dissolved copper behaviour (and indeed the behaviour of many other trace metals) in estuarine systems is not fully understood, but may be attributed to differences in sediment-water dynamics between systems and differences in the type and extent of organic complexation. It is still uncertain as to which DOC fraction trace metals are principally bound. If riverine copper is bound to high molecular weight humic acids, then co-removal of dissolved copper would be expected in the low salinity zone. This is clearly not the case in many estuaries and thus other processes must be operating. Another factor which should not be neglected is the temporal variation of both river flow and suspended sediment concentration. The kinetics of both adsorption and desorption reactions may also play a role. Most estuarine surveys reported in the literature are only 'snapshots' of chemical behaviour and usually do not take into account temporal variations.

| Table 2.2 | Dissolved copper behaviour in estuaries |
|-----------|---|
|-----------|---|

| Estuary | Behaviour | Reference |
|-------------------|--|-------------------------------------|
| Amazon, Brazil | Conservative, possible removal at low salinity | Boyle et al 1982 |
| Gota, Sweden | Conservative | Daniellsson et al 1983 |
| Maekong, Thailand | Conservative | Windom et al 1991 |
| Nile, Egypt | Removal in low salinity region | Abdel-Moati 1990 |
| Ogeechee, USA | Release at low salinity | Windom et al 1983 |
| Rhine, Holland | Extensive removal at low salinity | Duinker and Nolting 1978 |
| Severn, UK | Mainly conservative with anthropogenic inputs at high salinity | Apte et al 1990 |
| Savannah, USA | Release at low salinity and then some removal (very variable behaviour) | Windom et al 1983 |
| Scheldt, Holland | Release, mid-estuarine maxima | Van den Berg et al 1987 |
| Tweed, UK | Release at low salinity | Gardner and Ravenscroft 1991a, b |
| Tamar, UK | Release at low salinity, readsorption in the turbidity maximum, pore waters injputs at higher salinities | Ackroyd et al 1986, Morris 1986 |

Table 2.3 Dissolved copper concentrations in coastal and oceanic seawater

| Location | Concentration (µg/L) | Reference |
|--------------------------|----------------------|------------------------------|
| Great Barrier Reef | 0.22-0.32 | Denton and Burdon-Jones 1986 |
| New Jersey coast, USA | 0.18-0.39 | Yan et al 1991 |
| European shelf | 0.51 | Kremling 1985 |
| Cronulla, NSW | 0.08 | Apte et al 1996 |
| NE Pacific surface water | 0.037 | Coale and Bruland 1988 |
| N Pacific deep water | 0.172 | Bruland and Franks 1983 |

It is worth noting that the coastal and oceanic water concentrations of dissolved copper are typically an order of magnitude or more below estuarine concentrations, and are often below the detection capability of conventional analytical methods. Some typical values obtained using special protocols for sampling, sample handling and analysis are shown in table 2.3.

2.2.5 Particulate copper

The mean concentration of copper in the earth's crust has been estimated as 55 μ g/g (Taylor 1964), and Aston (1978) has suggested an average concentration in nearshore marine sediments of 48 μ g/g. Particulate copper concentrations in aquatic systems however, are very dependent on local geochemistry and contributions from anthropogenic inputs, so such generalisations are of limited use. An extensive survey of estuarine and coastal marine sediments in the South-East USA (Windom et al 1989) indicated copper concentrations of typically 1–20 μ g/g. Anthropogenic inputs may have a significant impact on particulate copper concentrations, for instance, the mean copper concentration in freshwater particulate matter from the River Rhine is 320 μ g/g (Duinker & Nolting 1978). Much lower copper concentrations (<50 μ g/g) were found towards the saline end of the estuary.

2.3 Copper in Macquarie Harbour waters

Macquarie Harbour waters have been the subject of recent extensive monitoring by DELM (Koehnken 1996). In addition, data from a four-day sampling trip in 1989 have been reported by Carpenter et al (1991). The latter study provides a snapshot of the distribution of dissolved copper, iron and organic matter in the harbour, and includes data for the King and Gordon Rivers. A summary of their results is presented in table 2.4.

| | Macquarie Harbour | Gordon River | Lower King River | Upper King River |
|--------------------------|----------------------|--------------|------------------|------------------|
| Dissolved Fe | 2.2 – 15 | 120 | 43 | 90 |
| Total Fe | 33 – 59 | 227 | 1120 | 101 |
| Dissolved Mn | 1.1 – 10 | 9 | 2860 | 6.5 |
| Total Mn | 14 – 39 | 12 | 3100 | 16 |
| Dissolved Cu | 2 – 7 | 0.5 | 31 | 0.1 |
| Total Cu | 4 – 11 | 0.3 | 430 | 0.9 |
| DOC ¹ (mg/L) | 1.2 – 2.7 | 5.2 | - | - |
| Cu complexation capacity | 0.1 - 4.3 | 8 | | - |

Table 2.4 Metals and organic matter concentrations (μ g/L) and copper complexation capacity ofMacquarie Harbour waters (from Carpenter et al 1991)

Results expressed as µg/L unless otherwise specified

1 dissolved organic carbon

A significant feature of the measurement to date is the relatively high dissolved copper concentrations measured in the surface waters of the northern harbour (7 μ g/L off Sophia Point)(figure 2.3). Although values higher than this have been measured in riverwaters, they exceed the solubility of copper at the pH and salinity of these waters, and can only exist in solution if complexed by organic matter, or bound to colloidal particles.

Measurements of dissolved organic carbon concentrations suggest that organic complexation of copper in the harbour waters is expected to be low. The concentrations of dissolved humic substances (and dissolved organic carbon) decreased linearly with salinity (conservative behaviour), with barely detectable concentrations at a salinity of 35‰. This was reinforced by very low copper complexation capacities in the harbour waters.

Dissolved iron measured in the lower King Riverwas low, but the total iron concentration (1.1 mg/L) was extremely high. At the time of the Carpenter et al study (1991), upstream waters of the King River, below the confluence of the Queen River and mine input, had pH of 6.9, a high dissolved iron concentration, and relatively low total iron and low copper concentrations. Compared to routine monitoring data in this region, the measured copper concentrations at this point are considered to be abnormally low (L Kochnken, pers comm).

In the King River downstream, the pH dropped to 5.3 as a result of either mine discharge or acid groundwater drainage from consolidated tailings along the river bank. At this point the total iron exceeded 1 mg/L and the dissolved iron was over 100 μ g/L. Copper was also elevated, in both dissolved and particulate forms. After mine closure the pH downstream was even lower than 5.3 (Koehnken 1996).

Particulate and dissolved iron loads of the magnitude seen in the King River are found in rivers in environments that have a naturally high iron mineralogy, or in those receiving mine discharge, such as the Ok Tedi in Papua New Guinea (Apte et al, unpublished results).



Figure 2.3 Map of Macquarie Harbour showing the general locations of the King River delta, the northern and southern Macquarie Harbour zones with sampling sites

In keeping with findings for the Ok Tedi (Apte et al, unpublished results), the behaviour of copper in the King River system is expected to be strongly influenced by the amount of dissolved organic matter. While this is particularly high in the Gordon River, there are no data to indicate the extent of complexation in the King, although it is believed that the total organic carbon content is considerably lower (L Koehnken, pers comm). This will be influential not only in complexing dissolved copper, but also in facilitating the release of copper from particulates.

A more comprehensive picture of the concentrations of copper in Macquarie Harbour waters can be obtained from the extensive data obtained by DELM both before and after mine closure. Results include data for both labile copper, as determined by anodic stripping voltammetry (ASV) at pH 5, and 'total' copper, defined as that measured in acidified, unfiltered samples. While the latter provide an indication of the mass flux to the harbour, the particulate copper can only be estimated from the difference between total and labile copper, and may in fact include a component of bound copper and copper associated with colloidal matter that would have been found in the dissolved phase.

The DELM data showed that high 'total' copper concentrations (>60 μ g/L) were generally found at stations closest to the King River delta, decreasing at more southern stations to below 20 μ g/L. In general, the stratification that has been reported in other reviews (Tong 1995) was mirrored by the total copper data, with highest copper concentrations in the surface layers. There were occasions where high total copper was measured in the bottom waters, but this was almost always associated with a high suspended sediment concentration, which was assumed to be copper rich. However, a high suspended sediment content of bottom waters was not always reflected in higher bottom copper concentrations.

The measurements of ASV-labile copper showed more consistent variability from top to bottom waters and from site to site. In the period September 1993 to November 1994, prior to mine closure, labile copper in surface waters of the harbour near the King River delta increased significantly from around 20 μ g/L to near 100 μ g/L in August 1994. 'Total' copper concentrations were generally more than double the ASV-labile values and showed a similar increase from July 1993. In southern waters, concentrations were typically below 6 μ g/L. These results are higher for the same sites than the total dissolved copper data reported by Carpenter et al (1991). In most cases the concentrations of copper in bottom waters were close to seawater concentrations, while middle and top water samples were high.

It would be expected that with the mixing of the freshwaters of the King River with the saline waters of the harbour, at low salinities a turbidity maximum might be evidenced with a steep decrease in suspended particulate copper in the water column. At the same time, dissolved copper would be expected to display conservative behaviour as a function of salinity. Measurements of total particulate and total dissolved copper as a function of salinity, as well as data for suspended sediment concentrations and information of the complexation and dissolution kinetics of copper are required. These should be obtained as part of the project on tailings chemistry.

The impact of mine closure on 'total' copper data can be seen from weekly monitoring data (Kochnken 1996). Immediately prior to mine closure on 12 December 1994, surface samples in the King River data showed copper concentrations at surprisingly lower values, of around 100 and 60 μ g/L respectively, than those measured in November 1994. After mine closure, copper concentrations generally increased, with excursions to over 400 μ g/L being noted, usually accompanied by a lowering of both pH and salinity.

These results also reinforce that the King River continues to be a source of colloidal and particulate copper, which will ultimately reach the sediments of Macquarie Harbour. Following cessation of riverine tailings discharge from the Mount Lyell mine in December 1994, the river waters have become more acid because the neutralising effect of the tailings (pH 9.5) on acid drainage is no longer present. The lower pH of the river waters appears to have caused considerable dissolution of iron, manganese and associated heavy metals, especially copper. Increased acidity may also reduce the extent to which removal of dissolved copper takes place

by adsorption on particulates in the mixing zone, although depending on how rapidly sedimentation was occurring these particles would still be seen in the 'total' fraction.

2.4 Copper in estuarine sediments

2.4.1 Geochemical speciation

Copper will be distributed in sediments in a range of geochemical forms. These will include weakly adsorbed copper that can be dissociated by ion exchange, copper bound to hydrous iron and manganese oxides, copper carbonates or insoluble sulfides, copper bound to organic matter, or copper in mineralised forms. Selective extraction methods have been used to quantify such associations (Kersten & Forstner 1989). Sequential extractions have been used to distinguish between ion-exchangeable metals, a carbonate fraction, a reducible fraction (hydrous oxides of iron and manganese), an oxidisable fraction (sulfides plus organic matter) and a residual fraction. These phases have usually been removed by magnesium chloride, acetate buffer pH 5, hydroxylamine hydrochloride/acetic acid, hydrogen peroxide/ammonium acetate, and a combination of strong acids, respectively. The selectivity of these separations is clearly operationally-defined, and further limited by the reprecipitation and readsorption that can occur as metals released from heterogeneous phases interact with other solubilised components, or with activated sediment surfaces (Rendell et al 1980). There have also been several attempts to relate the metal fraction ingested by organisms to that which is chemically extractable (Luoma 1983).

Sediment-bound copper will be in equilibrium with copper in the interstitial or pore waters. The equilibrium between dissolved free copper and the important adsorption sites on a sediment particle may be represented by :

$$= S_{(n)} - Cu \Leftrightarrow = S_{(n)} + Cu^{2+}$$

where: $[=S_{(n)}]$ is the concentration of sediment phase responsible for binding the metal, and $[=S_{(n)}-Cu]$ is the concentration of sediment-bound copper in equilibrium with the interstitial water.

In oxic sediments, the binding substrates may be hydrous oxides of iron and manganese or organic matter. For a given sedimentary binding substrate, the following ratio can be used as a surrogate measure of free metal ion concentration:

$$\frac{\left[=\mathbf{S}_{(n)}-\mathbf{C}\mathbf{u}\right]}{\left[=\mathbf{S}_{(n)}\right]^{*}\mathbf{K}_{1}}$$

where: K1 is a conditional equilibrium constant

It is important to recognise that only metal associated with the phase in equilibrium with the pore water metal concentration is being considered here.

In a study of lake sediments from the Canadian Shield (Bendell-Young & Harvey 1992) it was found that the value of the distribution coefficient, K_D , the ratio of the concentrations of sediment-bound copper to interstitial water lay between 0.9 and 1.9 L g⁻¹, which compares favourably to the by Martin and Whitfield (1981) calculated value of 0.83 L g⁻¹ for river waters and suspended sediment in the UK. Copper partitioning was independent of pH (p > 0.05) in lakes having a pH between 5.0 and 6.5. As has been shown by Benjamin and Leckie (1981), the adsorption edge for copper on iron oxyhydroxides occurs at around pH 5.0 for 30 µg/L Cu²⁺, and around pH 5.6 for 3 mg/L Cu²⁺. At least in the higher pH of estuarine sediments, there should be no pH effect on adsorption.

Instead of considering only one adsorption phase as controlling free metal ion in the interstitial water, it is probably more appropriate to consider multiple phases, which in oxic sediments amount to particulate organic carbon, and the hydrous oxides of iron and manganese (Luoma & Bryan 1981, Di Toro et al 1990). The equilibria described in equation 1 can be specified for any metal ion M^{n+} , in terms of each phase (EPA 1989):

eg
$$K_{Fe} = \frac{\left[=FeO_x - M\right]}{\left[=FeO_x\right]^* \left[M^{n+}\right]}$$
 3

$$K_{Mn} = \frac{\left[=MnO_{x} - M\right]}{\left[=MnO_{x}\right]^{*}\left[M^{n+1}\right]}$$

$$K_{POC} = \frac{\left[=POC - M\right]}{\left[=POC\right]^* \left[M^{n+}\right]}$$
5

In the presence of a number of complexing ligands, L_1 , L_2 , L_3 etc. in the pore water, the mass balance equation for the total metal in both the sediment and pore water will be:

$$M_{T} = (1 - \phi)([FeO_{x} - M] + [= MnO_{x} - M] + [POC - M]) + \phi([M^{n+}] + [ML_{1}] + [ML_{2}] + [ML_{3}] + ...)$$

where: M_T is the total concentration of desorbable metal per unit bulk volume of sediment and ϕ is the sediment porosity (Apte & Batley 1995).

Since the absolute quantity of metal in the pore water is very small in relation to the sorbed metal concentration, the mass balance equation can be simplified to the first term only. Incorporating the equilibrium equations 3–6, it is possible to show that:

$$\left[M^{a+}\right] = \frac{\left[M_{s}\right]}{K_{Fe}\left[=FeOx\right] + K_{Mn}\left[=MnOx\right] + K_{POC}\left[=POC\right]}$$
7

where
$$M_s = \frac{M_r}{(1-\phi)}$$
 and is the total sorbed metal per unit dry weight of sediment

The pore water metal concentrations are therefore theoretically predictable on the basis of measurable parameters, provided an accurate estimate can be made of the sorption constants.

The redox state of the sediments will be defined by the oxygen content of these waters, and typically at around 1–5 cm below the surface, the sediments become oxygen deficient. This will alter the chemistry of metals such as iron and manganese which in turn will affect the behaviour of metals such as copper that were previously bound to oxides of iron and manganese. Iron(III) hydrous oxides will be reduced to more soluble iron(II) species, while hydrous manganese oxides will be reduced to soluble manganese(II) species. Manganese, being more readily reduced, and less readily oxidised than iron, appears in the interstitial water column at a higher zone in the sediment. As oxygen is consumed, iron and manganese oxyhydroxides will be used to oxidise organic matter. The depth at which iron first appears will therefore be an indicator of the redox boundary.

Conversely iron(II) reacts with oxygen and is precipitated as iron oxyhydroxide (FeO(OH)), and because this reaction is rapid at natural pH values (Stumm & Morgan 1981), kinetic effects are unlikely to obscure the zero oxygen boundary. Higher iron and manganese concentrations may occur in surface pore waters than in overlying waters where the sediments are anoxic or suboxic (Pedersen et al 1993).

In anoxic sediments, the presence of framboidal pyrite has sometimes been observed (Skei 1988, Pedersen et al 1993), often within aggregates of organic matter. This results from the reaction of iron(II) with reduced sulfur species, and will only precipitate where sulfate is present with reduced sulfur species.

The oxic-anoxic boundary usually exists fully within the sediment layer, but may also occur within the water column and may often move between water and sediment, driven by natural cycles. For some dynamic systems steady-state conditions may not apply because the changes in the redox boundary occur faster than those in the chemistry. For example, the rate of oxidation of manganese is slower than that of iron, hence it is more readily transported through oxic environments.

For copper associated with particulate phases in oxic sediments, log K_D values typically lie in the range 1–2 in the pH range 6–8. In anoxic sediments, the extreme insolubility of copper sulfide (log K_{sp} = -40.9 as covellite), means that copper will be effectively immobilised. Mineralised copper as sulfide would be expected to be relatively immobile in anoxic sediments, but surface reactions may result in a slow dissolution of some copper in the oxic zone.

2.4.2 Copper bioavailability in sediments

Campbell et al (1988) considered the bioavailability of metals from sediments in terms of two types of organisms, type A being organisms living in intimate contact with the sediment, but not capable of ingesting it such as benthic algae and rooted aquatic plants, and type B organisms able to ingest sediment and take up metals from the particulate phase such as benthic invertebrates. Type A organisms respond to labile metal in the interstitial water.

The bioavailable fraction may be a small proportion of the total sediment copper concentration, and selected extractants have been used in attempts to separately quantify this fraction. Good correlations have been obtained for lead and zinc accumulated from contaminated sediments by gastropods, crabs, polychaete worms and snails, with the fraction extractable with either EDTA or dilute acid (Ying et al 1993). These reagents are able to strip away surface coatings leaving the more inert and mineralised fractions. Normalising the acid-extractable concentration with, for example, the extractable iron concentrations has been used to improve the correlation with metal uptake by a number of species (Luoma & Bryan 1978, Tessier et al 1984), where the metal-binding substrates are dominated by, in this instance, hydrous iron oxides. In the case of seagrasses, good correlations have been obtained for a range of heavy metals with those extracted from the sediment by diethylenetriamine pentaacetic acid (DTPA) (Lee et al 1978).

The behaviour of iron and manganese in lake sediments is important in defining metal bioavailability to benthic biota. Andrews and Fitchko (1987) showed that the main sources of metals to benthic tubificids were those associated with iron and manganese oxides rather than organically-bound metals. Copper associated with manganese oxides was found to be 100 times more bioavailable than copper associated with iron oxides or organics (Luoma & Jenne 1977). Both of these species are likely to be dissociated by EDTA, and possibly also dilute acid extraction.

Organisms which burrow in the sediments to breed or feed will be exposed to the elevated concentrations of copper that interstitial waters may contain. The bioavailability of copper metals will be related to the free, or 'labile' copper ion concentration (Morel 1984, Cowan et al 1986, Campbell et al 1988). This concentration will be controlled by pH, redox potential (Eh) and dissolved organic matter, as it is in surface waters.

The bioavailability of sediment-bound metals can be more readily predicted, provided some consideration is given to the concentrations of free, acid-volatile sulfides (AVS) in the solid phase (Allen 1993). The concentrations of many heavy metals in pore waters are controlled by sulfide. It has been shown that added cadmium, for example, can react with the pool of AVS, to form insoluble cadmium sulfide, which is apparently not bioavailable (Di Toro et al 1990). This reaction involves the dissociation of iron monosulfide to Fe²⁺ and S²⁻. Heavy metals such as copper, zinc, lead and cadmium form sulfides which have lower solubility than that of FeS.

Sulfide present in the form of FeS therefore has the ability to detoxify added heavy metals, and sulfide already tied up with other heavy metals is notionally unavailable to detoxify further metal inputs. It is necessary, therefore, during the measurement of AVS to also determine the concentration of metals already present as sulfides. If the ratio of the concentration of these simultaneously extractable metals (SEM) to AVS is less than one, then toxicity is unlikely. If the ratio is greater than one, then there may be toxicity. It should be noted that iron is also present in sediments as pyrite, FeS_2 , but the mild acid treatment used in the measurement of AVS does not release its sulfur.

The above findings have been confirmed in laboratory studies, where the toxicities of sediments due to metals such as cadmium and nickel is the same when normalised to AVS (figure 2.4), but this has not been verified in the field. The difference between AVS and SEM is the quantity of sulfide present as FeS that is available to detoxify added metals (Hare et al 1994), and is therefore a more useful measurement. Ultimately the pore water copper concentrations must be judged against the water quality criteria to determine the likelihood of toxicity.

High dissolved organic carbon concentrations in the pore waters will reduce toxicity because in general complexed metals will be less toxic than free metal ions except in the case of lipid-soluble organic species. Burrowing animals have the ability to oxygenate anoxic sediments and in the microenvironment of their burrows, the dissolved concentrations of metals can be significantly altered. These animals can also translocate sediments, bringing them to the surface and altering the vertical stratigraphy. It should also be noted that the root systems of plants oxygenate the sediments in their immediate environment thus modifying the chemistry of both the sediments and their interstitial waters.



Figure 2.4 Organism mortality as a function of the ratio of extractable cadmium and nickel to acid-volatile sulfide (Di Toro et al 1992)

In examining the Macquarie Harbour sediments, key measurements will involve the identification of sediments that contain clevated copper concentrations and then the sampling of pore waters in these locations to ascertain the extent of mobilisation. The mineral component of the sediments may have the ability to buffer pore water copper concentrations. For example, the high carbonate content of some mine overburden would prevent acidification arising from sulfate-reducing bacteria. Measurements of metal concentrations should be accompanied by sulfide and dissolved organic carbon analyses.

2.5 Copper in Macquarie Harbour sediments

The earliest comprehensive study of copper in sediments from Macquarie Harbour, including the King River mouth and delta, was undertaken by the Department of the Environment in 1975 (Department of the Environment 1975). A selection of their copper data is shown in table 2.5, and is compared with results of surveys in January 1986, and May 1993 (Koehnken 1996). As expected, highest copper concentrations were observed in King River sediments. Concentrations were lowest in sandy sites, especially on the north western side of the harbour (data not shown).

A feature of the data is an apparent increase in sediment copper at most sites over the eighteen year period, although it is difficult to be sure that the exact locations are being compared in each case. An evaluation of the analytical procedures used for the 1975 data, suggest that their nitric acid digestion adequately releases all copper from a standard mining residue, thus eliminating analytical techniques as the reason for elevated levels in the later samples.

| Location | | Total Conner | |
|------------------|-------------------|-------------------|-------------------|
| Location | 1975 ^ª | 1986 ^b | 1993 ⁵ |
| King River mouth | 1980 | - | . — |
| King River delta | 1300 | | _ |
| Near Strachan | 750 | 1200 | 1250 |
| Northern harbour | 690 | 850 | 1030 |
| Northern harbour | 460 | 880 | 1100 |
| Northern harbour | 720 | 520 | 540 |
| Mid harbour | 810 | - | 1310 |
| Mid harbour | 910 | - | 570 |
| Mid harbour | 900. | _ | 1120 |
| Southern harbour | 710 | _ | 1120 |
| Southern harbour | 310 | | 860 |
| Southern harbour | 330 | - | 310 |

Table 2.5 Total copper concentrations (μ g/g) in surface sediments from Macquarie Harbour

a Department of Environment 1975

b Koehnken 1996

The other significant finding is that copper concentrations are elevated even in the southern harbour, and although mining activities did take place in this region at the turn of the century, it is unlikely that this contamination would persist in surface sediments. It is more likely that, as indicated by the copper concentrations in water, transport and deposition of particulate copper from the King River inflow has been actively occurring throughout the harbour.

In almost all cases, sediment copper concentrations where shown to decrease with depth, but typically by only around 30% over a depth of 20 cm. At many of the northern harbour sites, copper contamination extends to depths in excess of 1 m (Koehnken 1996), implying a sediment accumulation rate in excess of 1 cm/y, which is not uncommon in a water body of this nature. The influence of bioturbation in disturbing these sediments is considered to be limited, given that the high copper content is likely to have a significant biocidal action, a conclusion reinforced by an observed absence of worms or other bioturbating organisms in these sediments.

The concentrations of copper in almost all cases exceeded accepted sediment quality guideline values (table 2.6). Data for other metals (Department of Environment 1975, Kochnken 1996) showed that the surface concentrations of zinc (200–300 mg/kg) and lead (70–118 mg/kg) are close to the accepted sediment quality guideline values, while these are exceeded by copper (table 2.6), as well as by mercury (100–250 μ g/kg). The major source of mercury is not the Mount Lyell mine, but appears to be a component of natural minerals in the catchments of rivers entering the southern harbour. Background mercury concentrations of 240 μ g/kg and above are not uncommon for lake sediments, while many contaminated estuarine sediments have values in excess of 1 mg/kg (Forstner & Wittman 1979).

An examination of the relationship between copper and iron concentrations in harbour sediments revealed a linear correlation ($r^2 = 0.71$), indicative of the dominant role of iron in copper binding. The implication is that much of the copper is present as coatings on hydrous iron oxide particles, aggregated from solution, via colloids. The correlation between manganese and copper was not as significant ($r^2 = 0.53$).

As has already been discussed, the bioavailability of copper and other heavy metals in sediment pore waters will be controlled by the redox status of the sediments and by the presence of an excess of acid-volatile sulfides, which are able to complex heavy metals as insoluble sulfides. Data on the redox profiles of Macquarie Harbour sediments show that the clay-silt copper-rich sediments are typically oxic only to a depth of 2–6 cm. Below that the negative redox potential is indicative of an anoxic environment (Koehnken 1996).

Measurements of metal concentrations in sediments sampled in May 1993, were also accompanied by AVS measurements (Koehnken 1996).

These showed clear examples where the SEM/AVS ratio exceeded one, but where the excess of exchangeable metals could vary by as much as an order of magnitude. For example in the southern harbour core there was a high excess metal concentration in the low sulfide surface sediment (36.9 nmole) which was still maintained in the higher sulfide layer in the same core

| | Washingt | on State | US | SA | Flo | rida | Nethe | rlands |
|---------|--------------------------------------|----------|--------------------------------------|-----|--------------------------|------|--|--------|
| Metal | Ginn & Pastorok 1992 ^a | | Long and Morgan 1990 ⁵ | | MacDonald et al 1992° | | Van der Kooij et al 1991 ^d | |
| | SC | MCL | ERL | ERM | NOEL | PEL | τv | IV |
| Copper | 390 | 390 | 70 | 390 | 30 | 170 | 36 | 190 |
| Zinc | 410 | 960 | 120 | 270 | 70 | 280 | 140 | 720 |
| Lead | 450 | 530 | 35 | 110 | 25 | 170 | 85 | 530 |
| Mercury | 0.41 | 0.59 | 0.15 | 1.3 | 0.15 | 1.4 | 0.3 | 10 |

Table 2. 6 Summary of sediment quality criteria for metals (mg/kg)

* SC = screening criteria, adverse effects not likely; MCL= maximum contaminant levels, require investigation or cleanup

^b ERL= effects range low, adverse effects 10% of the time; ERM= effects range median, adverse effects 50% of the time

NOEL= no observed effects level ; PEL= probable effects level

TV= threshold value; IV= intervention value

at 6–9 cm, but a smaller excess in the surface sediments in cores from the more northern sites (2-10 nmole). It is likely that the pore water copper concentration in the southern harbour core would be much higher than for the most northern sites and therefore poses a greater environmental risk in terms of metal bioavailability, despite similar SEM/AVS ratios. The protocols for measuring AVS as well as the field significance of such measurements are however still the subject of active research programs in our own laboratories and elsewhere.

2.6 Pore waters and sediment processes

2.6.1 Pore water sampling and analysis

Pore waters are the critical pathway by which metals are transported into and out of the sediments. An analysis of pore water copper concentrations as a function of depth in the sediments provides information from which copper fluxes can be calculated. The sampling of pore waters without altering their chemistry is technically difficult. Although in the past pore waters have been separated from sediments in the laboratory by squeezing, centrifugation or solvent displacement (Batley & Giles 1979), such processes destroy the fine structure of the sediment yielding a mean pore water concentration, while also potentially altering the speciation of trace elements in the sample. In addition, when applied to sectioned cores, they do not provide sufficient water on which the required analyses can be performed. *In situ* sampling overcomes these problems.

Early designs of *in situ* samplers allowed suction of pore water from prescribed depths, but more recently the use of multi-chambered dialysis samplers has permitted sampling as a function of depth, with equilibration achieved between the sediment and membrane-enclosed water.

The most commonly used pore water samplers, first described by Hesslein (1976), were used initially for nutrient analysis. The first application to metal analysis was described by Carignan (1984) and Carignan et al (1985). The Carignan 'peeper' consist of a 30x15x1 cm acrylic plastic plate in which 6.5x3.6x0.6 cm chambers spaced 1 cm centre to centre are machined. The plate is covered with an appropriate dialysis membrane kept in place by a 0.2 cm thick acrylic sheet with apertures matching the chambers, and fastened to the main body by nylon screws 15 cm apart. Prior to use, the chambers must be filled with distilled water and, if being used with anoxic sediments, should be deoxygenated by placing in acrylic cylinders filled with distilled water and bubbling with nitrogen for 24 hours. For sampling, the peepers are inserted into the sediment by hand, and left in place for a week before removal.

The peeper used by Di Toro et al (1990) was made of unshrunk cast acrylic sheet, 15.2x7.6x5.1 cm deep, with six rows of three 1.9 cm diameter, 3.8 cm deep holes, each with a volume of about 5 mL. The samples from the three horizontal cavities were combined to give a total volume of 15 mL, sufficient for electrochemical measurement of dissolved cadmium. The open side was covered by a sheet of 1 mm polycarbonate (Nuclepore) followed by a 0.076 cm low density polyethylene gasket and a 1.3 cm cover plate, having the same hole pattern as the body, and secured with PVC cap screws and nuts. Equilibration time was determined to be less than 1 day when seawater was used in the peeper chambers.

Multi-chambered peeper designs (eg figure 2.5) are essential where fine structure in a sediment profile is being studied. The optimal peeper design (Teasdale et al 1995) represents a compromise between several requirements:

• the peeper chamber volume, V (cm³), must be sufficiently large to allow all required analyses to be made;

- the exchange surface area of the chamber window, A (cm²), should be large enough to minimise the influence of sediment heterogeneity;
- the sampling interval, I (cm), of the chambers in the vertical plane should be small enough to provide depth profiles of sufficient resolution;
- insertion of the peeper should cause minimal physical and chemical disturbance to the sediments; and
- the time for equilibration of the water in the peeper chambers with the external pore water should be acceptably short.

The equilibration time is governed by the design factor, F (cm), which is defined as V/A, with low F values resulting in more rapid equilibration. With these requirements in mind we designed and used a peeper with chambers that have windows on both faces (F=1.0) which results in >90% equilibration being achieved within 3 days. The sample volume with this design is 7.7 mL per chamber, although by using two rows of chambers in a wider peeper, this volume can be doubled to 15 mL.

Peeper lengths have ranged from 30 cm to over 1 m. The length of peepers used is determined by the depth in the sediment and the height in the overlying water that is of interest. Generally, most processes of interest occur within 10 cm either side of the sediment/water interface.



Figure 2.5 Multichambered acrylic peeper 30x8x2 cm, (a) plan view, (b) side view (drawing not to scale)

Polymethylmethacrylate (acrylic, Perspex, Plexiglass) has been preferred to other materials for peeper fabrication because it is relatively inexpensive, mechanically strong, and readily machineable. A significant problem with the use of plastics arises from their oxygen content. Oxygen may be released from the plastics in quantities and at rates that are sufficient to oxidise Fe(II) and Mn(II) in anoxic pore waters resulting in the formation of iron and manganese oxyhydroxide colloids which eventually form precipitates (Carignan 1984). The colloidal material will re-dissolve upon acidification of the sample (the sample preservation step) resulting in anomalously high values for dissolved iron and manganese. The dissolved concentrations of non-redox-active species may also be altered by coprecipitation or adsorption onto the metal oxyhydroxide surfaces. For this reason, plastic peepers need to be thoroughly deoxygenated before use.

Carignan (1984) noted that almost all plastics are more or less permeable to oxygen and that diffusion of oxygen from within the acrylic body can be important in anoxic waters. Carignan et al (1994) stated that the ideal polymer for peeper construction should either have a very low oxygen solubility or a very long half-life for oxygen release. As a consequence, they compared the release of molecular oxygen from a range of materials and concluded that none of the materials tested had those desirable qualities. They recommended that acrylic peepers be deoxygenated for up to 30 days by placing in an inert atmosphere before assembly. After assembly, a further 48 hours deoxgenation was advised. Other plastics, polycarbonate in particular, may be more suitable because they deoxygenate more rapidly than acrylic, while having similar mechanical properties, although they seem to always give lower concentrations of iron and manganese, even if deaerated (Carignan, pers comm).

In practice, problems caused by oxygen release appear to be most significant in systems that have low reductant concentrations, such as oligotrophic lakes. In other systems such as estuaries, reductant species (eg sulfide), if present in high enough concentrations, are able to scavenge oxygen.

The choice of membrane material is also important. Polysulfone membranes are generally preferred to cellulose dialysis membranes as they are resistant to bacterial degradation (Carignan et al 1985). Typically, 0.20 or 0.45 μ m pore size membranes are used, though speciation information, based on size-fractionation, can be obtained by using membranes with smaller pores.

It is recommended that new peepers be initially cleaned in detergent solution (to remove any oil or grease from the machining process). Before use peepers and membranes should be soaked in dilute nitric acid (eg 10% v/v) for a few days to remove trace metals. Following thorough rinsing of all components with deionised water and deoxygenation, the chambers should be filled with deoxygenated, deionised water and the membranes secured in place by a plastic faceplate. Care must be taken not to include any air bubbles in the chambers. This is best avoided by assembling the peepers in a water bath of deionised, deoxygenated water. The screws used to assemble the peepers should ideally be plastic. Nylon screws are commonly available but tend to soften when wet. Stainless steel screws may be acceptable provided they are first checked as a source of contamination.

Preserving the deoxygenated status of the peepers during transport from the laboratory to the field is then necessary and this generally involves the use of containers filled with deoxygenated water. Oxygen-barrier bags (eg Saran[™]) are suitable for this purpose.

Precipitation of iron (and manganese) oxyhydroxides can be a problem with peepers if suitable precautions are not taken. It is important that peepers removed from anoxic sediments be sampled and acidified as soon as possible after removal from the sediments, otherwise air diffusion into the compartments will precipitate iron on the inner surfaces, carrying with it trace metals. Tessier et al (1989) noted that, when used in lake sediments, precipitation of iron oxyhydroxides occurred just below the sediment-water interface in a few peeper compartments. This was postulated as arising from the downward diffusion of oxygen meeting the upward diffusion of iron(II). In the case of zinc, Tessier et al (1989) calculated large positive concentration gradients near the sediment-water interface of acid lakes (pH <6), typically $0.6-2.6 \times 10^{-4}$ mol cm⁻³ cm⁻¹. At higher pH (>6) lower concentration gradients were observed, $0.1-0.3 \times 10^{-3}$ mol cm⁻³, and could be negative or positive.

The solution transport of species in pore waters is slower than in open waters owing to the effects of sediment porosity along with the absence of strong currents. This is counteracted by chemical processes such as dissolution and desorption, biological activity (eg bioirrigation and bioturbation) and in some systems, pore water flow. These factors will vary temporally, spatially and with depth. In view of the complexity of the system, it is hard to recommend equilibration times for peepers with a great degree of certainty. As an approximate guide, equilibration times of about two weeks have been typical for Hesslein-style peepers (Teasdale et al 1995). Site-specific evaluations of equilibration times are strongly advised.

The diffusion of species across the membrane into the peeper chambers will act to reduce their concentrations in the pore waters adjacent to the membrane (C_0). The concentration of C_0 will be replenished by diffusional transport from surrounding pore waters (known as drawdown) and may be supplemented by desorption and dissolution processes. The relative importance of dissolution and desorption will be dependent on the chemical species in question and the kinetics of the relevant dissolution and desorption reactions. If these are significant, then equilibration will be more rapid.

Some idea of the importance of factors such as the size and volume of peeper chambers on equilibration rates may be obtained through mathematical modelling (Brandl & Hanselmann 1991). For a peeper immersed in a water column, the concentration of a particular solution species (C_i) in a peeper compartment at time t (s), may be estimated by :

$$t = \frac{F}{2} * \frac{1}{k_{M}} * \ln\left(\frac{C_{0}}{C_{0} - C_{i}}\right)$$
8

where C_0 is the concentration of the species in the pore water, F is the design factor, and k_M (cm.s⁻¹) is a measure of the rate of transport across the membrane, as determined by the diffusion conditions in the sediment. It should be noted that this equation describes the rate of concentration change in the peeper chambers only approximately.

Teasdale et al (1995) demonstrated the importance of F in determining the time required for equilibration, using data for K^+ , and concluded that varying F is the most practicable way in which equilibration rates can be influenced.

Peepers must be deployed with minimum disturbance to the sediment layer. A sound knowledge of the sampling site in terms of its physical topography and general sediment chemistry is also advisable, otherwise the peeper data may not be representative of the sampling location. Peepers can be hand-deployed in shallow waters, however at deeper locations, the use of a diver is usually necessary. In order to aid retrieval, the location of the peeper can be marked by a buoy, submersed tag or a guideline secured to the bank.

When a peeper is removed from the sediment, it must first be cleaned thoroughly in order to prevent the ingress of sediment particles into the chambers which can easily happen when the membrane is pierced during sampling. High pressure water-pistols can be used to effectively clean the surface. The rate of oxygen diffusion from the atmosphere into the chambers is quite high (4 μ M min⁻¹) and may result in iron oxyhydroxide precipitation (Fe(II) is oxidised rapidly at ambient pH levels, $t_{V_2} = 2.34$ min at pH 8; $t_{V_2} = 2.34$ min at pH 7). The chambers must therefore be sub-sampled as soon as possible (within 20 min), in order from the anoxic to the oxic end of the peeper. Sampling in a glove box filled with an inert atmosphere (eg N₂) is preferable, especially if speciation information is required. Sample preservation by adding acid directly into each chamber is not recommended as this will lead to remobilisation of any adsorbed or precipitated metals.

The chambers are sub-sampled by piercing the membrane with a plastic micropipette tip and withdrawing the sample. Acidification is the preferred method of sample preservation for total metal analysis, although this is clearly unsuitable for measurements of pH, Eh and sulfide. The volume collected from each chamber is typically 5 to 8 mL.

The combination of low sample volume and sub-ppb to low ppb concentrations of many metals makes the analysis of pore water samples extremely challenging. Multi-clemental analysis methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) (for major ions, Fe and Mn) and ICP-mass spectrometry (ICP-MS) are ideal for fresh waters. Alternatively, graphite furnace atomic absorption spectrometry (GFAAS) is an appropriate analytical technique given its low sample volume requirement (20 μ L) and sub-ppb detection limits for most metals. Flame AAS may be applied to the determination of Fe and Mn, which are present in pore waters at low ppm concentrations providing sufficient sample volume is available.

For the accurate analysis of saline samples or low level determination in freshwaters, GFAAS or ICP-MS are not entirely satisfactory and some form of matrix separation/preconcentration step is usually required (eg solvent extraction). Such approaches are made difficult by the low sample volumes and potential for interferences from high iron, manganese and dissolved organic carbon (DOC) concentrations. A thorough validation of analytical methods is therefore advisable. Similar problems are encountered when applying electrochemical techniques such as anodic stripping voltammetry.

2.6.2 Application of pore water peepers to sediment process studies

Pore water peepers have been used in a number of studies of chemical processes in sediments (eg Brandl & Hanselmann 1991, Carignan et al 1994). Our own studies using pore water peepers in estuarine waters in Sydney and New Zealand, and in water bodies in the Ok Tedi and Fly River systems in Papua New Guinea (Batley et al 1993), have yielded profiles of iron, manganese and heavy metals such as copper which have provided a valuable understanding of the chemical processes in the sediments. Typical dissolved metal profiles across the sediment/water interface obtained with peepers are shown in figure 2.6. The variability between peepers deployed at the same site is relatively small for major ions (usually around $\pm 10\%$) but higher for the redox-active elements such as iron and manganese. Such variability is most likely the result of spatial heterogeneity within the pore waters and is greatest in the top few centimetres of sediment. Nevertheless, depth profile trends are usually quite consistent between peepers deployed at the same site.

Although we have assumed a reasonably constant concentration of metals in pore waters over the time required for peeper equilibration, this may not be the case in systems where concentrations undergo cyclic changes (eg tidal systems, rivers). The validity of applying peepers in such systems will depend on the timescale and magnitude of the variations occurring relative to the time required for peeper equilibration. In some cases, the lengthy equilibration times required by peepers may be a disadvantage. Polyacrylamide gel samplers (Davison et al 1991, Davison & Zhang 1994) which have short equilibration times, may be a useful alternative, although these samplers have yet to be fully validated in field situations.

Riverine transport brings copper in both dissolved and particulate forms to the estuarine mixing zone. In this region flocculation of iron occurs as hydrous iron(III)-oxides. These can adsorb dissolved copper and then undergo sedimentation and ultimate burial in bottom sediments, along with waterborne particulate copper. When sediment containing these particles becomes anoxic, particulate and dissolved copper will form highly insoluble CuS. Iron(III) in particulate hydrous oxides will be reduced to soluble iron(II) which enters the pore waters and is able to diffuse to the overlying waters. If these are sufficiently oxic, oxidation, reprecipitation and scavenging of soluble copper can occur. Copper bound to these oxides in the sediments will be released and either precipitate as CuS, or diffuse through the oxic zone with Fe(II). These reactions of soluble species in the pore waters will be altered by the presence of dissolved organics that will bind and stabilise copper in solution, and particulate organic matter that may also affect copper speciation in the solid phase.



Figure 2.6 Pore water profiles of iron and manganese in sediments from the Georges River, Sydney, NSW

The extent of the oxic/anoxic mixing zone in both the water and sediment layers and the effect on it of tides and water movement generally, will all impact on the fluxes of both copper and iron in the system. The reactions close to the sediment surface therefore play a critical role in governing the ultimate fate of copper.

This complex picture may be further exacerbated by burrowing benthic biota which are able to introduce oxygen deep in anoxic sediments and maintain an oxic environment by pumping in oxygenated water. This gives rise to oxidation processes in zones where they might otherwise have been absent.

Diffusional fluxes can be computed using Fick's first law (Lerman & Brunskill 1971, Ulman & Aller 1982) when the concentration gradient at the sediment-water interface is known, and with corrections being made to diffusion coefficients to simulate sediment tortuosity (Berner 1980). However, Davison (1985) cautioned that the estimation of fluxes of elements from concentration profiles assumed to be diffusion-controlled is unwise. The dynamic nature of water bodies means that instantaneous steady-state profiles may miss rapid cycling of elements or fluxes from transient events that can often only be seen by sampling over very small intervals. Nevetheless many studies have used depth profiles in pore waters and overlying water to calculate diffusional fluxes.

Approaches have been made to the calculation of diffusional fluxes that attempt to take into account not only the pore water concentration-depth profiles, but also the extent and rate of sorption and desorption reactions on particles, in both the sediment and water layers (Nyffeler et al 1984).

In previous studies we have seen examples where copper fluxes have gradients both into and out of the sediments. In Macquarie Harbour, although the deeper waters overlying the sediments have a lower dissolved copper content than the surface waters, it is likely that the concentrations are still sufficiently high that the net transport of copper is into the sediments. Although these sediments have a high copper content, it is likely that even in the anoxic sediments the pore water copper concentrations will be lower than that of the overlying water.

2.6.3 Copper flux measurements using benthic chambers

It has been argued that the use of pore water profiles gives an indirect estimate of diffusional flux, but does not quantify the role of bioturbation and mechanical mixing (Ciceri et al 1992). More accurately put, peepers reflect the pore water concentration profiles which have developed over times ranging up to months and years, the timescale being set by the time for equilibrium being established between diffusional loss from the sediments, *in situ* production, and bioirrigation/bioturbation. Since bioturbation and mechanical mixing are essentially random in space and time, the porewater profile captured by the peeper is some sort of average value covering only the immediate vicinity of the peeper. In addition, peepers lack spatial resolution at the sediment-water interface, precisely where the concentration gradients are greatest and the zone of most direct relevance to the calculation of fluxes.

It was decided to use both benthic chambers and peepers to maximise the information that might to obtained from sediment fluxes. Benthic chambers, developed initially for measuring nutrient fluxes in the deep sea, offer an alternative approach (Berelson & Hammond 1986, Berelson et al 1987, Buchholtz-Ten Brink et al 1989, Jahnke & Christiansen 1989, Santschi et al 1984). They isolate a known volume of seawater covering a well-defined (and known) area of the sediment surface. Changes over time in physical and chemical parameters within the chamber are measured directly *in situ*, or by periodically sub-sampling a fixed volume

which is replaced by water from the immediate external environment of the chamber. In our chamber about 700 cm of sediment surface is enclosed and the total volume (dependent upon depth of penetration) is about 10 L. Within the chamber, transfers across the sediment/water interface are dominated by processes occurring immediately beneath the surface and the results reflect the impact of bioturbation and bioirrigation as well as the diffusional flux over the time of the deployment (Berelson et al 1990a, b).

A key element in the design and construction of benthic chambers is the means adopted to ensure adequate stirring. It should be sufficient to ensure that the chamber is well-mixed, and that the diffusive boundary layer is realistically represented (this requires a priori knowledge of the surface roughness and current, and often a representative value is adopted). Stirring should not be so vigorous, however, that the sediment surface is eroded and the underlying pore water mixed into the chamber. Booji et al (1991) have noted that in sandy sediments, the flow induced by the stirring can augment the inherent natural diffusive flux of material from the sediments. These effects are not present in muddy sediments (Booji et al 1994).

We have attempted to design a system which avoids these pitfalls and have been helped in this endeavour by sceing the automated benthic chamber developed by Dr Will Berelson (University of Southern California, Los Angeles) as part of the CSIRO Port Phillip Bay Environmental Study. Advice and assistance has been given also by Andy Longmore (Victorian Fisheries Research Institute) who is building another variant of the Berelson Benthic Chamber.

2.6.4 Plastic strip collectors in sediment process studies

Belzile et al (1989) showed that Teflon strips, immersed in lake sediments for many months, accumulated deposits of iron and manganese oxides at the oxic/anoxic boundary. This occurred because the plastic contains oxygen which diffuses to the surface and causes deposition of soluble reduced iron and manganese at the point where the diffusive oxygen flux exceeds the dissolved sulfide concentration. We have since shown (Allen et al 1995) that both polycarbonate and Teflon have this ability. In fact polycarbonate or Lexan has a higher oxygen content which, if the strip is immersed in the sediment for a period of up to two weeks, leads to deposition of hydrous iron oxides along the full length of the strip below the oxic/anoxic boundary (figure 2.7). With time, the excess of sulfide over diffusing oxygen leads to a retraction of the oxide layer closer to the boundary (figure 2.7). The time to achieve the equivalent of the deposit on Teflon is around 12 weeks.



Figure 2.7 Effect of deployment time on the deposition and mass of iron-oxyhydroxide collected on polycarbonate strips immersed in an estuarine sediment

It is possible to analyse the depth profile of the iron deposit not only for iron, but for codeposited heavy metals, such as copper. The use of a frame which contains 1 cm wide polycarbonate strips stacked one above the other, facilitates dissolution of discrete intervals of the deposit. The deposition of iron and metals simulates the process that might occur by the introduction of oxygen at depth into the anoxic zone of the sediments. The strips effectively freeze the pore waters at a particular depth by altering the redox status.

The application of these collectors has yet to be extensively evaluated. We have conducted studies in local estuaries and have results that are consistent with data from peepers and sediment speciation analyses (Allen et al 1995). It was felt this would also provide useful additional information on Macquarie Harbour sediments.

3 Methods

3.1 General analytical procedures

For this study the measurement of copper concentrations in sediments employed the following general analytical procedures, unless otherwise stated. All acids used were of ultrapure grade (Normatom) and all water was deionised (Milli-Q). All other reagents were of analytical grade. All bottles (Nalgene) used in the sampling and preparation program were made from low density polyethylene with leak-proof lids. All sampling equipment was soaked at least twice for a minimum of 24 hours in 10% (v/v) nitric acid, then three times in water before drying in a Class 100 clean room and preparing for use.

Where in-line filters and syringes were used, the syringes were acid-washed as described above. Before filtering a sample, the syringe was used to pass 15 mL of 2% (v/v) nitric acid through the membrane, then two 20 mL volumes of water, followed by 20 mL of the sample to be filtered. Then the sample aliquot was filtered and collected in a suitable container. Membrane filters used with vacuum filtration apparatus were cleaned in a similar manner.

All samples were analysed with appropriate numbers of blanks and standards according to accepted analytical quality control methods. Limits of detection were calculated at three times the standard deviation of the blank samples.

3.2 Field program

Two field trips to Macquarie Harbour were conducted. The first took place from 19–25 June 1995 and the second from 17–22 July 1995. Following a review of the available data, and after consultation with Dr Lois Koehnken from DELM, ten sites of primary interest were selected. These are shown in figure 2.3 and included one site in the entrance to Long Bay (site 1), three sites in the vicinity of the King River delta (sites 2–4), five sites spaced approximately equidistantly along the east coast of the harbour, between the mouths to the King and Gordon Rivers (sites 5–9), and a western harbour site (site 10). The co-ordinates of these sites and the water depth observed during the first field trip are shown in table 3.1.

During the first field trip, divers collected 250 mL samples of both surface and bottom waters from each site. These samples were analysed for dissolved and particulate metal concentrations, salinity, total suspended solids, and some were used for ultra-filtration and complexation capacity studies. At the time of sample collection, and on every other day that a site was visited, measurements were also taken of temperature, salinity, pH, turbidity, dissolved oxygen and redox potential using a Hydrolab Water Quality Meter supplied by DELM.

| Site | Location | Depth |
|------|---------------------------|-------|
| | latitude, longitude | (m) |
| 1 | S42°10'188", E145°19'213" | 10 |
| 2 | S42°11'224", E145°20'425" | 5–6 |
| 3 | S42°10'942", E145°21'065" | 5–6 |
| 4 | S42°11'541", E145°20'361" | 6 |
| 5 | S42°13'222", E145°21'137" | 10 |
| 6 | S42°16'556", E145°23'551" | 10 |
| 7 | S42°19'564", E145°26'110" | 11 |
| 8 | S42°22'187", E145°29'522" | 14–15 |
| 9 | S42°22'522", E145°31'043" | 11 |
| 10 | S42°18'880", E145°18'748" | 1112 |

Table 3.1 Peeper and stacker deployment sites

Sediment pore water samplers (peepers) (Teasdale et al 1995) were assembled ready for use at the CSIRO Centre for Advanced Analytical Chemistry, Lucas Heights, and shipped to Strahan with the other sampling equipment. A diagram of the peeper design used is shown in figure 2.5. Duplicate peepers were deployed in the sediments by divers at each of the sites. and marked by an anchored buoy with guidelines going from the buoy line to each peeper. Four of the peepers used were 100 cm long and the remaining sixteen were 30 cm long. The 100 cm peepers were used to provide information on pore water copper concentrations deep in the sediment. One was deployed at each of sites 3, 5, 6 and 7. The peepers were retrieved after five or six days. This was sufficient time for them to have attained near-equilibrium with the sediment porc waters, as was verified by the pore water concentration profiles obtained. Sediment particles were removed from the peepers with a jet of harbour water from a 'super-soaker'. The chambers were then sub-sampled on the boat, using pipettes with acidwashed tips, and the sample stored in 8 mL bottles ready for return to Lucas Heights. These samples were analysed for metal concentrations to obtain a profile of the pore water and overlying water concentrations across the sediment-water interface, from which benthic fluxes could be calculated.

Lexan (polycarbonate) collectors, assembled as separate 1x5 cm strips stacked one above the other in a Perspex frame, were also deployed at each site and marked in the same fashion. A diagram of the 'stacker' design used is shown in figure 3.1. The stackers were retrieved during the second trip to the site in July, cleaned in a manner similar to the peepers and returned to Lucas Heights for analysis of the iron-oxyhydroxide deposits, and associated trace metals, collected on the strips. Concentration-depth profiles of the collected metals were obtained.

Replicate sediment cores were collected by divers using 60 cm long PVC coring tubes. Sampling locations were within 20 m of the peepers and stackers. One core from each site was sealed and frozen in a rock-salt ice-bath after collection to preserve the redox status of the sediment. Profiles of particulate metal concentrations and selected samples of acid-volatile sulfide (AVS), simultaneously extracted metals (SEM) and particle size fractionation were obtained from this core. The other core was sectioned at the site to enable a physical description of the sediment together with depth profile measurements of pH using a potentiometric electrode (Activon).
Seven sets of sediment traps, made from PVC water pipe (27 cm by 9 cm ID), were deployed around the harbour during the first visit and recovered during the second. The locations of these deployments, the number of traps at each site, the deployment and recovery dates, and the water depths are given in table 3.2. The site locations are also shown in figure 2.3. The mass and particulate metal concentrations of the collected sediment were determined for each trap, allowing sedimentation fluxes to be calculated for each site.



Figure 3.1 Design of the polycarbonate (Lexan) strip collectors used in this study

Table 3.2 Sediment trap deployment sites

| Site ¹ | Location, | Number of | Date | Date | Depth |
|-------------------|----------------------------|-----------|----------|-----------|-------|
| | latitude, longitude | traps | aepioyea | recovered | (m) |
| 2 | mouth of King River | 10 | 20.6.95 | 22.6.95 | 22.4 |
| | S42°11'181", E145°20'139" | | | | |
| 2 | mouth of King River | 10 | 22.6.95 | 24.6.95 | 22.4 |
| | S42°11'181", E145°20'139" | | | | |
| 3 | north of King River mouth | 5 | 22.6.95 | 17.7.95 | 10 |
| | S42°10'269", E145°19'650" | | | | |
| 5 | off Connellys Point | 6 | 22.6.95 | 17.7.95 | 20 |
| | \$42°13'085", E145°20'939" | | | | |
| 10 | Liberty Bay | 5 | 22.6.95 | 19.7.95 | 10 |
| | \$42°18'856", E145°18'655" | | | | |
| 11 | northwest of Coal Head | 10 | 22.6.95 | 17.7.95 | 50 |
| | \$42°18'364", E145°22'888" | | | | |
| 12 | north of Grummett Island | 9 | 22.6.95 | 19.7.95 | 20 |
| | S42°22'352", E145°27'214" | | | | |

1 these deployments have been designated site labels the same as those in table 2.1 if they are within ≈500 m

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Benthic chambers (figure 3.2), constructed at the Centre for Environmental Mechanics, were deployed at four sites around the delta area (table 3.3, figure 2.3) during the second trip to Macquarie Harbour (June 1995). Measurements of dissolved oxygen, pH and temperature were made within the chamber at 15 minute intervals, and sub-samples were collected for heavy metal measurements. Oxygen consumption rates and benthic fluxes were calculated from these data. An aliquot of D_2O was injected at the start of each deployment to determine chamber volume and to estimate sediment diffusivity.

| Site ¹ | Location | Date | Deployment duration |
|-------------------|-------------------------|---------|---------------------|
| 2 | S42°11'01", E145°21'04" | 17.7.95 | 7 |
| 2 | S42°11'23", E145°20'36" | 18.7.95 | 7 |
| 4 | S42°12'55", E145°21'20" | 19.7.95 | 27 |
| 5 | S42°13'23", E145°21'20" | 21.7.95 | 25 |

Table 3.3 Benthic chamber deployment sites

1 these deployments have been designated site labels the same as those in table 2.1 if they are within ≈500 m

3.3 Sample preparation and analysis

3.3.1 Overlying water samples

The 250 mL overlying water samples were sub-sampled the day after collection, with about 20 mL being syringe-filtered through 0.45 μ m in-line membrane filters (Sartorius) into a 30 mL sample bottle. These were then acidified to pH 2 with 40 μ L of nitric acid and stored in a refrigerator. Another 15 mL was filtered through the same membrane into a 25 mL glass bottle, sealed with aluminium foil and also stored in a refrigerator. The remainder of the unfiltered sample was also refrigerated.

The filtered and acidified water samples were analysed for total dissolved iron, manganese, potassium and silicon by inductively coupled plasma atomic emission spectrometry (ICP) after dilution with 0.1% (v/v) nitric acid to minimise matrix suppression. Total dissolved copper was measured using a graphite furnace atomic absorption spectrometer (GFAAS) following a micro-solvent extraction procedure (Apte & Gunn 1987). Dissolved organic carbon (DOC) was measured on the unacidified, filtered sample, that had been stored in glass, using an Anatoc organic carbon analyser (SGE).

Salinity was measured on a portion of the unacidified, unfiltered water sample using a YSI Model 33 S-C-T Meter. An aliquot of unfiltered water was filtered through a pre-weighed 0.45 μ m membrane, which was then dried in an oven at 110°C for 24 hours, cooled to room temperature in a desiccator and re-weighed. The particulates were digested in 5 mL of nitric acid and 1 mL of hydrogen peroxide under low power conditions in a commercial microwave oven. The sample was then diluted ten-fold with water and analysed for heavy metals by ICP and for copper by GFAAS.

Selected unacidified 0.45 μ m filtered samples were ultra-filtered through a 0.025 μ m membrane, to remove some of the colloidal fraction. The filtrate was acidified to pH 2 with nitric acid and analysed for copper by GFAAS after micro-solvent extraction.

Copper complexation capacity and labile dissolved copper measurements were also carried out on selected samples. Sample aliquots were pipetted into polarographic cells. Each sample aliquot was then spiked with copper over a range of concentrations from 0 to 100 μ g/L. The





Figure 3.2 Two views of benthic chamber deployed in 10 m of water, southwest of the mouth of the King River, Macquarie Harbour, Tasmania. The hyperdermic syringe is used for removing samples from the chamber. Note the buildup of sediment in a short time (less than 10 hours)

aliquot with no spike added was also used for the labile copper measurement. These solutions were then allowed to equilibrate overnight before supporting electrolyte was added. Differential pulse anodic stripping voltammetry measurements were then performed with a hanging mercury drop electrode using a BioAnalytical Systems BAS 100B Voltametric Analyzer. The resulting copper titration curve for each sample was analysed using the Van den Berg/Ruzic graphical method that assumes complexation can be described by a single ligand (Apte et al 1988).

3.3.2 Pore water samples

At Lucas Heights, the peeper subsamples were acidified to pH 2 with nitric acid and let stand overnight to dissolve all the oxyhydroxide precipitate and heavy metals. ICP was used to measure iron, manganese, potassium and silicon, after performing a suitable dilution to minimise saline matrix suppression effects. Copper concentrations above 50 μ g/L could also be reliably measured with ICP in this fashion. Low level copper analyses were undertaken using a specially developed micro-solvent extraction procedure prior to measuring with GFAAS (Apte 1996 unpub).

3.3.3 Stacker samples

The Lexan strips were removed from the stacker and cleaned thoroughly with water. Each strip was then placed in a 15 mL centrifuge tube. The iron oxyhydroxides and associated heavy metals collected on each strip were dissolved in 10 mL of 7% (w/v) ascorbic acid solution by shaking the samples for 24 hours. This was then acidified to pH 2 with nitric acid to solubilise all heavy metals and was shaken for another 24 hours. These solutions were then analysed for heavy metals by ICP.

3.3.4 Sediment cores

Frozen sediment cores were cut with a band saw into 3 cm sections and were then further cut in half. One half of each core section was stored in the freezer for AVS and SEM measurements. The other half was allowed to thaw and was used for particle size fractionation and particulate metal analysis.

Each sediment section selected for AVS and SEM measurements was allowed to thaw within a nitrogen-filled glove bag and weighed into a round-bottom flask, which was then attached to an AVS distillation rig (Allen et al 1993). Upon acidification with H_2SO_4 and after stirring, H_2S gas was evolved. This was purged into a NaOH_(aq) trapping solution with oxygen-free nitrogen carrier gas, where it was stabilised as $S^{2^-}_{(aq)}$. Sulfide concentrations were measured using the methylene blue colorimetric method of Allen et al (1993). Sediment moisture content was determined on separate sub-samples. The SEM released during the AVS dissolution procedure, were determined by ICP.

Total particulate metals were determined on each core section. The sediment samples were dried at 110° C for 24 hours and then homogenised with a mortar and pestle. About 100 mg dry weight of sediment was accurately weighed into a polycarbonate bottle and 2 mL nitric and 4 mL hydrochloric acids were added. This solution was left to stand overnight before being digested for 20 minutes in a commercial microwave oven at low power. After cooling to room temperature, the final solution volume was made up to about 100 mL and the metal concentrations measured by ICP. A sample of PACS-1 standard reference material (National Research Council, Canada) was analysed in every batch as a quality control measure. The certified value for particulate copper in PACS-1 is 452 mg/kg. The mean recovery obtained in this study was 90±6%.

Sediment size fractionation was performed on selected samples by wet sieving sediment through 180 and 63 μ m mesh stainless steel sieves. Three fractions (>180 μ m, 180–63 μ m and <63 μ m) were collected and dried for 24 hours in an oven at 110°C. The samples were then allowed to cool in a desiccator before each fraction was weighed and calculated as a percentage of the whole sediment sample.

3.3.5 Sediment traps

Sediment accumulated in the traps was collected on a 0.45 µm membrane, freeze-dried and weighed at room temperature. The particulates were then digested in 5 mL nitric acid and 1 mL hydrogen peroxide under low power conditions in a commercial microwave oven. The sample was then diluted fifty-fold with high purity water and analysed for all heavy metals by ICP.

3.3.6 Benthic chambers

Analyses for heavy metals were conducted on samples collected during the benthic chamber experiments. Because of problems with filtration equipment, these samples were unable to be filtered on site. Instead they were stored at 4° C without filtration. Upon receipt at Lucas Heights, each sample was divided into two portions. One portion was acidified with nitric acid to pH 2, let stand for 24 hours and then filtered, and the other was filtered first and then acidified with nitric acid to the same pH. This treatment was to allow the role of oxyhydroxide precipitation in the inadequately preserved samples to be determined. Samples were then analysed for heavy metals by ICP after a suitable dilution to avoid matrix suppression. Copper was measured by GFAAS following a micro-solvent extraction (Apte & Gunn 1987).

4 Results and discussion

4.1 Macquarie Harbour waters

4.1.1 Water column profiles

An indication of the high degree of stratification of Macquarie Harbour waters was obtained from Hydrolab casts performed at each site. Water column profiles of temperature, pH, salinity, dissolved oxygen, redox potential and turbidity are shown in Appendix 1. At most sites, bottom waters were more saline, lower in dissolved oxygen, warmer and less turbid compared with the surface waters. Gradients in pH were generally small, except for some days at sites 2 and 4 in the King River delta where there was a significant difference in pH between the surface and bottom waters. All of these findings are consistent with previous data (Tong 1995, Koehnken 1996) and confirm the presence of different layers of water in Macquarie Harbour. However, it is worth noting that this data represents the most intensive measurement schedule reported to date, with several measurements being made at each site over a week. This enabled the daily variation at each site to be estimated.

Generally, at least two distinct bodies of water were observed; a brackish water body (4–10%) overlying a water body with salinity approaching that of seawater (25–30%), with the interface between the two layers often being quite abrupt. Occasionally, on the delta, shallow layers of freshwater would lie atop the brackish layer (site 2, 19 and 20 June, and site 4, 19 June). At site 3 on 25 June the surface water was over 20‰ salinity, but even here there was a more saline layer beneath the surface. Occasionally there were up to four layers of water apparent (site 8, 20 June) including a substantial one beneath the top layer, with salinity 10–15%. These observations are in general agreement with the pattern of water circulation for Macquarie Harbour proposed by Koehnken (1996). Furthermore, the presence of a layer of intermediate salinity (10–20%), which was proposed to play an important role in this water circulation model, was only observed on one occasion during this study (Appendix 1).

These results indicate that the day to day variation in the water column at many of the sites, particularly those in the vicinity of the King River delta, are considerable. The delta sites show very high variation in all parameters measured. This reflects tidal effects and also the changing volume of water coming down the King River as regulated by the power station (Koehnken 1996). These changes will have a significant effect on the heavy metal chemistry in these waters and the dissolved copper concentration could vary substantially as a result. It is important to be aware of this when considering the concentrations of copper and other elements in the overlying water presented in the following section, as samples were taken on one day only during the field trip. A more comprehensive picture of the variation in the water column chemistry of these elements will be provided in the report of project 14.

4.1.2 Dissolved and particulate metal concentrations in the water column

Results for the analysis of dissolved copper, iron, manganese, silicon, DOC and salinity in 0.45 μ m filtered surface and bottom water samples, are shown in table 4.1. For comparison, dissolved metal concentrations for the Gordon and King Rivers, at various locations and under various conditions, obtained from other studies are shown in table 4.2. Copper, iron and manganese levels in the particulate (>0.45 μ m) fraction and the total suspended solids are shown in table 4.3. It should be noted that the convention of describing the constituents of a water sample that pass through a 0.45 μ m filter membrane as being 'dissolved' and those that do not as being 'particulate' have been used in this study. However, it is important to be aware that this is an arbitrary distinction and that there will often be colloidal material present in the dissolved fraction.

A comparison of the metal concentrations between forms (ie dissolved vs particulate), sites (ie northern, 1 to 5, vs southern, 6 to 10) and water depths (ie surface vs bottom) helps to provide an understanding of the processes operating in Macquarie Harbour. Copper is predominantly found in the dissolved (<0.45 μ m) fraction (65–85%) at all sites and depths, which suggests that this is the dominant phase in which copper is transported around the harbour. Some exceptions were noted where total suspended solids (TSS) were high, reflecting the particulate copper loading of this material.

| Site | Sample | Cu | Fe | Mn | Si | DOC | Salinity |
|------|----------|--------|--------|--------|--------|--------|----------|
| | location | (µg/L) | (µg/L) | (µg/L) | (µg/L) | (mg/L) | (‰) |
| 1 | surface | 99 | 330 | 183 | 730 | 4.8 | 6.3 |
| | bottom | 17.3 | 33 | 35 | 386 | 1.2 | 22.0 |
| 2 | surface | 145 | 360 | 292 | 800 | 3.7 | 5.0 |
| | bottom | 99 | 256 | 209 | 880 | 4.0 | 9.3 |
| 3 | surface | 560 | 1040 | 880 | 1060 | 2.4 | 0.5 |
| | bottom | 25.5 | 53 | 35 | 387 | 1.4 | 21.8 |
| 4 | surface | 420 | 600 | 860 | 960 | 0.3 | 4.5 |
| | bottom | 33.5 | 62 | 35 | 370 | 1.5 | 22.0 |
| 5 | surface | 119 | 257 | 172 | 690 | 4.7 | 6.5 |
| | bottom | 13.0 | 51 | 38 | 321 | 0.3 | 23.3 |
| 6 | surface | 16.2 | 214 | 33 | 700 | 7.6 | 5.5 |
| | bottom | 8.5 | 27 | 21 | 328 | <0.3 | 24.0 |
| 7 | surface | 17.4 | 211 | 39 | 690 | 8.2 | 5.5 |
| | bottom | 10.8 | 42 | 37 | 363 | 1.1 | 22.5 |
| 8 | surface | 14.1 | 232 | 32 | 730 | 8.5 | 5.0 |
| | bottom | 4.7 | 16 | 24 | 372 | 0.6 | 26.5 |
| 9 | surface | 11.5 | 240 | 26 | 790 | 9.5 | 4.3 |
| | bottom | 4.0 | 20 | 29 | 374 | 4.4 | 23.8 |
| 10 | surface | 42 | 156 | 26 | 790 | 10 | 9,3 |
| | bottom | 5.0 | 39 | 52 | 420 | 2.6 | 25.8 |

Table 4.1 Dissolved metals, DOC and salinity in the <0.45 μm filtered fraction of Macquarie Harbour waters

1 DOC: dissolved organic carbon

| Location | Conditions | Cu | Fe | Mn | Reference |
|--------------|---------------|------------------|--------|--------|-----------------------------|
| | | (µg/L) | (µg/L) | (µg/L) | |
| Gordon River | _ | 0.3 ^a | 120 | 9.0 | Carpenter et al 1991 |
| Upper King | - | 0.1 | 90 | 6.5 | Carpenter et al 1991 |
| Lower King | initial flush | 7000 | 8500 | **** | O'Grady & Featherstone 1995 |
| Lower King | high flow | 600 | 1000 | - | O'Grady & Featherstone 1995 |
| Lower King | low flow | 600 | 1200 | - | O'Grady & Featherstone 1995 |

Table 4.2 Dissolved metal concentrations (µg/L) obtained from other studies

a the authors suspect that this value may be high due to contamination

Table 4.3 Particulate metals and TSS in the >0.45 μm filtered fraction of Macquarie Harbour waters

| Site | Sample | Cu | Fe | Mn | TSS ¹ |
|------|----------|---------------------|---------------------|---------------------|------------------|
| | location | (µg/L) ² | (µg/L) ² | (µg/L) ² | (mg/L) |
| 1 | surface | 40 | 530 | 4.8 | <2.8 |
| | bottom | 11 | 340 | 7.2 | 7.7 |
| 2 | surface | 67 | 690 | 2.3 | <2.8 |
| | bottom | 47 | 980 | 4.8 | <2.8 |
| 3 | surface | 27 | 3230 | 6.4 | 28.4 |
| | bottom | 20 | 1010 | 11 | <2.8 |
| 4 | surface | 430 | 4300 | 8.1 | 21.3 |
| | bottom | 80 | 2680 | 23 | 24.3 |
| 5 | surface | 30 | 289 | 2.6 | <2.8 |
| | bottom | <4.4 | 58 | 3.8 | <2.8 |
| 6 | surface | <4.4 | 31 | 1.8 | <2.8 |
| | bottom | <4.4 | 80 | 5.8 | <2.8 |
| 7 | surface | <4.4 | 38 | 9.6 | <2.8 |
| | bottom | <4.4 | 41 | 5.5 | <2.8 |
| 8 | surface | <4.4 | 22 | 2.4 | <2.8 |
| | bottom | 9,9 | 310 | 49 | 21.6 |
| 9 | surface | <4.4 | 45 | 5.2 | <2.8 |
| | bottom | <4.4 | 139 | 18 | <2.8 |
| 10 | surface | 7.7 | 78 | 26 | <2.8 |
| | bottom | <4.4 | 77 | 35 | <2.8 |

1 TSS: total suspended solids

2 these units are used because TSS was below the detection limit at most sites, therefore the

conventional units for particulate metal concentrations (µg/g) could not be used

Manganese was also present predominantly in the dissolved fraction, with over 90% in the surface waters and over 70% in the bottom waters passing through a 0.45 μ m filter. The surface water and northern harbour manganese concentrations are significantly higher than for the bottom and southern harbour waters respectively.

The behaviour of iron was somewhat different. For the northern harbour sites most of the iron is in the particulate fraction, in both the surface and bottom waters. The percentage decreases somewhat at sites 1 and 5, which are further from the King River. Iron is predominantly in the particulate fraction in the bottom waters of the southern harbour sites also. However, in the surface waters for the southern harbour sites, most of the iron is in the dissolved fraction. This could indicate that the colloidal-sized iron material remains in suspension and is transported all around the harbour in the surface waters. On the other hand, particulate iron material in the surface waters for the southern harbour sites could be due to sediment suspension or coagulation of material in the water column.

A plot of dissolved copper, iron and manganese versus salinity (figure 4.1), using the data in table 4.1, clearly demonstrates that there are significant removal processes operating in the low salinity (<5‰) regions of the estuary, as has been shown in a previous study (O'Grady &

Featherstone 1995). Although there are freshwater inputs other than the King River contributing to the low salinity of surface waters, particularly in the southern harbour (Koehnken 1996), which have the potential to confound the results, the dissolved copper concentrations indicate that King River water is reaching southern sites, and with increasing salinity copper removal occurs. Over the salinity range from 0-5%, copper concentrations dropped by almost an order of magnitude from a high of over 550 µg/L and continued to decrease with increasing salinity. The change is accompanied by a similar decrease in dissolved iron from over 1000 µg/L and manganese from over 800 µg/L. Each of these metals are most likely present as colloids, with the copper being coprecipitated or adsorbed onto <0.45 µm colloidal iron and manganese oxyhydroxides. The removal mechanism occurring at about 5‰ salinity is well established and involves aggregation of colloids into 'particle'-sized material or the coating of existing particles, thereby removing them from the 'dissolved' fraction. These particles may then precipitate out of the water column, which is probably why the proportion of copper to manganese in the <0.45 µm remains about the same, as the total concentrations in the water column decrease.

Ultrafiltration of the 0.45 μ m filtered surface water samples from sites 1 and 4, through a 0.025 μ m filter, removed 50–80% of the dissolved copper. This supports the idea that colloidal species are responsible for the high dissolved copper concentrations, as true dissolved species should pass through this pore size. Not all colloids will be removed by filtration through 0.025 μ m pores either, so the proportion is possibly even higher.

A closer inspection of the plot of dissolved copper vs salinity reveals five points that appear to be outliers. These points correspond to the surface waters for the southern harbour sites (6 to 10), which have the five lowest copper concentrations in the 4-10 % salinity range, and actually show a trend in which copper concentration increases with salinity. These points are plotted in figure 4.2, along with the Gordon River dissolved copper concentration obtained from table 4.2. This trend reflects the relative concentrations of these metals in the Gordon River compared with the harbour and is typical of that for a situation in which the receiving water is the source of a contaminant and the river draining into it acts as the diluent. The high residence time for dissolved constituents in the harbour, particularly for the surface waters, is demonstrated by this observation. Note however that there is still evidence for removal processes occurring in these waters. There is no significant correlation with the DOC and the copper levels at these sites, although the former are higher at these sites than the northern ones. The manganese concentrations for the surface waters at these sites follow a similar trend to copper. The iron concentrations at these sites, on the other hand, do not deviate significantly from the dilution plot with the King River. This is due to the iron concentrations in the King River far exceeding those in the Gordon River (table 4.2).

The plots in figure 4.1 indicate that the metals behave in a similar manner. Therefore, some degree of covariance was therefore expected. A reasonable coefficient of determination was observed between dissolved copper and iron ($r^2 = 0.86$) for all sites and an even better one between dissolved copper and manganese ($r^2 = 0.97$), as shown in figure 4.3. Koehnken (1996) also reported a strong correlation between dissolved copper and manganese in the King River, but the correlation between copper and iron was poor. The improved correlation of copper with iron in this study is likely to be due to the controlling influence of iron chemistry in the buffered, higher salinity harbour waters. These conditions are likely to produce combined iron and manganese oxyhydroxide colloids so that even if the copper is chemically associated with the manganese, it will still correlate well with iron.



King River

Macquarie Harbour



Figure 4.1 The variation of dissolved copper, iron and manganese with salinity at sites 1 to 10



Gordon River Macquarie Harbour

Figure 4.2 The variation of dissolved copper with salinity at the surface of sites 6 to 10 and the Gordon River, with Gordon River and Macquarie Harbour as end members

The role of dissolved organic carbon (DOC) in the speciation of dissolved copper is also important. It is well known that natural organic matter can bind copper in forms that are less toxic than free ionic forms (Batley 1995). The DOC concentrations in the harbour are towards the upper end of the normal range for estuaries, with values of 5-10 mg/L in the surface waters. The higher values are found in the southern waters because the Gordon River is the main source of DOC.

The ability of DOC to bind copper is generally measured as the copper complexation capacity. There are many ways in which this can be estimated and depending upon the method chosen, complexes having conditional stability constants within a particular window of values will be measured (Apte et al 1988). Measurements of copper binding with only strong ligands in Macquarie Harbour waters have been reported by Carpenter et al (1991). They found that copper complexation capacities had values that were only about half those of the measured dissolved copper concentrations, which had serious implications for the toxicity of copper in the harbour. However, there are many other weaker ligands, likely to be present, which are capable of binding copper to the extent that they may ameliorate its bioavailability. As part of this study, we examined several water samples for copper complexation capacity were undertaken using anodic stripping voltammetry at the natural sample pH. This technique measures the complexation capacity of both weak and strong ligands.





Figure 4.3 Correlation of dissolved copper with dissolved iron and dissolved manganese at sites 1 to 10

| Site | Sample location | Labile copper (µg/L) | Dissolved copper ¹ (µg/L) | Residual copper complexation capacity (µg/L) |
|------|--------------------|-------------------------|---|---|
| 1 | surface | 30 | 99 | <0.1 |
| 9 | surface | <0.1 | 12 | 31 |
| 9 | bottom | 2.7 | 4.0 | <0.1 |
| 10 | surface | 14 | 42 | <0.1 |
| 10 | bottom | 3.1 | 5.0 | <0.1 |

Table 4.4 Complexation capacities of Macquarie Harbour waters

1 from table 3.1

It is immediately apparent from these results that in the high copper-containing samples, ie the surface waters at sites 1 and 10, all of the available organic ligands are complexed by copper or other metals. Site 1 surface waters are predominantly King River waters. At site 9, the southernmost site, on the other hand, surface waters are much lower in total copper and a residual complexation capacity (31 μ g/L) was observed. This is much greater than the complexation capacity measured previously by Carpenter et al (1991) who found values of 1.0-4.3 μ g/L in Macquarie Harbour and 8 μ g/L in the Gordon River. The difference is probably due to inclusion of the complexation capacity of weaker ligands in the method used for this study. The bottom water at site 9 is predominantly ocean water.

The low dissolved copper concentration measured in surface waters at site 9 means that there is excess complexation capacity at this site and thus there is no detectable labile copper. However, at the other sites measured where the DOC and dissolved copper concentrations vary with dilution (table 4.1), the copper concentrations generally exceed the complexation capacity. Thus labile copper was measured at these sites and it is expected that most of the waters in the harbour experience similar conditions. Therefore, although a greater range of ligands were included in this study, a significant proportion of the dissolved copper was labile, which means it is potentially bioavailable.

4.2 Macquarie Harbour sediment

4.2.1 Physical characterisation of the sediment

Sediment cores from sites 1 to 10 were examined for texture and other key characteristics, including any detectable odour of hydrogen sulfide. These descriptions are given in table 4.5. The particle size fractionation for various depths at each site are shown in figure 4.4.

The field observations of particle size and the presence of sulfide were in good agreement with subsequent lab measurements and are mostly consistent with zones of the harbour sediments described in a previous report (Department of the Environment 1975). The zones identified in the latter study are given in figure 4.5. The most notable differences between this and our study were at sites 7 and 10. In the 1975 study, site 10 was reported as being sandy, but little sand was found in any of the cores taken at site 10 in our study. It is known that fish farming activities had commenced at this site between the two sampling dates for this difference and may have been responsible for the differences. On the other hand, site 7 was described as being a brown ooze, but in our study was found to be predominantly sand. The 1975 study did indicate a small area north of site 7 which was sandy, so it is possible that this type of sediment is now more widespread along that part of the harbour than in 1975. These differences are most likely due to local variation in the vicinity of each site and the difficulties of interpolating between sites. They may also represent real changes in the dispersal and sedimentation patterns in the harbour over the interim period, however there is insufficient evidence to establish this with certainty.

| Site | Depth | Sulfide | Texture | Other details |
|------|------------------|---------|-------------------------------------|--|
| 1 | top | none | very fine ooze | brown & grey layers inter-mixed in top & |
| | middle | | more consolidated & clayey | middle, grey bottom |
| | bottom | | still clayey, more cohesive | |
| 2 | top | none | very fine ooze | brown/grey layer at top, becoming more |
| | middle | | some consolidated, cohesive | grey with depth, becoming more |
| | la a 66 a ma | | lenses | consolidated with depth also, some |
| | Dottom | | lavers of ooze | present |
| 3 | top | none | mostly silts & clays, some fine | brown layer at top, chocolate brown & |
| - | | | sandy grains | grey streaks gradually becoming more |
| | middle | | alternating cohesive lenses, with | grey with depth, sand particles most often |
| | | | glittering flecks, & ooze | in cohesive lenses |
| | bottom | | mainly very fine ooze, | |
| | | | consolidated, dewatered | hanna lavas at tas, ab sastata basun 9 |
| 4 | top | none | ooze, very fine | brown layer at top, chocolate brown & |
| | midale | | non-cobesive material | grey with depth |
| | bottom | | fine & highly consolidated | groy war ocpan |
| 5 | ton | none | noorly cobesive oozy | chocolate brown layer right at surface |
| 5 | bottom | none | verv fine & smooth, guite | then duller brown, then grey brown at |
| | 0000 | | consolidated | depth, low organics |
| 6 | top | none | very fine material, cohesive | a number of distinct horizons evident, |
| | middle | | shell fragments & organic matter | brown colour at top, grey colour at 10–15 |
| | | | abundant, less cohesive | cm, and sand at bottom, becoming |
| | bottom | | quite sandy, also silt & clay, | coarser with depth |
| | | | lustrous minerals, shell fragments, | |
| _ | | | conesive | |
| 7 | 0–5 cm | none | medium sand, some silt | very sandy and brown, sediment difficult |
| | 5-10 10-15 | | | to extrude from tube, no conesion |
| 8 | 0_2 cm | low | mostly silt & clay, some sand | coarser than 9 & 10, 0–7 cm with definite |
| U | 0-2 GH | 101 | plastic & cohesive | sand sized particles, some of which were |
| | 2–5 | | n | lustrous, possibly being pyrite; 7-13 cm |
| | 5–7 | | 18 | some vegetation matter and shell |
| | 7–13 | | " | fragments at depth; |
| | 13–14 | | slightly larger grain size | 15-16 cm dark sediment |
| | 14-15 | | some small shell fragments | |
| | 16-17 | | 11 | |
| | 17–18 | | п | |
| | 18–19 | | u | |
| | 19–20 | | fine lustrous grains | |
| | 20-21 | | | |
| | 21-22 | medium | " | |
| 9 | 03 cm | medium | silt & clay, extremely fluid | grittiness, possibly due to organics, very little cand: 7–8 cm black sediment |
| | 3-0 5-7 | | silt & clay | inde sand, 7-0 cm black sediment |
| | 7-8 | | silt & člav | |
| | 89 | | silt & clay | |
| | 9 —10 | | silt & clay, very fine sand | |
| | 10–15 | v. high | cohesive | |
| | _ | | silt & clay, more cohesive | 1 1 11 stransform to the |
| 10 | 0–1 cm | medium | silt & clay, very fluid | colour gradually changing from chocolate |
| | 1-2 | | siit & clay, more conesive | prown to grey/black over top 9 cm continued to get darker with depth after |
| | ∠4 46 | | silt & clay, more conesive | this: 8–10 cm high organics, no sand. |
| | 6-8 | | silt & clay | very fine |
| | 8-10 | medium | silt & clay | - |
| | 10-12 | to high | silt & clay | |



Figure 4.4 Particle size fractionation with depth at sites 1 to 10

Sediment at sites 1 to 5 was mostly made up of particles <63 μ m in diameter, which fits the description of brown ooze given in the 1975 report. This material is of King River origin, both from river-borne particulates as well as through deposition from solution in the mixing zone of the estuary. Sites 6, 7 and 8 had larger sized particles (>63 μ m), particularly at depth, with site 7 being predominantly >180 μ m at all depths. A notable trend at site 6 was the increase in the proportion of <63 μ m particles towards the surface and a corresponding decrease in >180 μ m particles. This trend is probably due to an increase in the deposition of King River material over time at this site, which may be due to an extension of the range of



Figure 4.5 Areas of sediment types in Macquarie Harbour (after Department of the Environment 1975, map 4)

deposition. When considered along with the small proportion of $<63 \mu m$ particles at site 7, a limit to the dispersal of particulate matter from the King River along the eastern shore of the harbour is implied, with this limit being between sites 6 and 7.

The fine particles at the southernmost sites (8 and 9) are probably characteristic of sediments typical for Macquarie Harbour before the Mount Lyell mine began releasing tailings material; the black colour and presence of sulfide being very different from the sediment of King River origin. As such, it is likely that this sediment has the Gordon River or other inputs as its ultimate source. The sulfide characteristics and the colour of the site 10 sediments suggest that

they are also predominantly from this source, although they may be intermingled with particles from the King River, most of which appear towards the surface as if they are more recent deposits. The change in colour of the sediment from brown to black with increasing depth suggests this. This observation also suggests a recent extension of the range of deposition of the King River material. This phenomenon may be related to the construction of the power station on the King River and the subsequent change in the discharge of the river, although there also may have been some impact of the construction of the Gordon Power Station.

4.2.2 Metal concentrations in the sediment

Depth profiles of copper, iron and manganese in the sediment cores are shown in Appendix 2. An important feature of these results is the depth to which the high copper levels extend in the delta region, as has been indicated in previous work (Koehnken 1996). The sediment concentrations of copper at all of the northern harbour sites (1-5) easily exceed all of the probable effects guideline concentrations which, depending on the sediment quality guidelines considered, lie between 170 and 390 mg Cu/kg (Batley 1995). The surface layers of the other sites, with the exception of site 7, also exceed these levels although most of the concentrations fall below this level at depth in the sediment.

Sites 1 to 5 show similar profiles, with very high concentrations of iron, manganese and copper and very little change in concentration with increasing depth. The only apparent trend is a slight decrease with depth in the copper concentration at sites 1 and 5, which are the farthest of these sites from the King River. The concentration of copper at these sites are also slightly lower in general than the delta sites indicating that some dilution of the particulate copper concentration occurs with dispersion, as might be expected.

At site 6 the copper concentrations are elevated in the surface scdiments but decrease to below the sediment quality guideline levels at about 8 cm depth. A similar trend is observed for the manganese profile and the iron profile also decreases with depth although it does not level off until about 20 cm. Comparison of these profiles with the particle size fractionation for this site indicates that a relationship may exist in which the heavy metal concentrations decrease with increasing particle size. This is a well established phenomenon (Luoma 1990) and is due to the greater surface area of smaller particles and also their chemical nature, both of which act to facilitate the adsorption of heavy metals.

Site 7 shows a very different profile from all other sites. The copper concentrations in the surface sediments are much lower than at other sites (140 mg/kg) and do not change significantly with depth. They are actually lower than the sediment quality guideline values indicated above, although they do approach the lower limit of these values. Again, a relationship with the particle size fractionation, with predominantly coarse sands present at site 7, seems likely. These observations indicate that there is very little material of King River origin that is deposited at this site, which may be representative of an extensive section along the eastern shore of Macquarie Harbour.

Site 8 shows similar concentrations to site 7 below a depth of about 5 cm. Above this however the copper concentrations rise sharply to exceed the guideline levels. Iron and manganese have similar profiles. Once again, a relationship with the particle size fractionation at this site seems likely, with a higher proportion of fines (< 63 μ m) present in these surface layers, although the sand is generally smaller than at site 7, being mostly in the 63–180 μ m range at depth. This profile implies that there has been a recent change in conditions that have brought about an increase in copper concentrations in the surface sediments. However, we have insufficient knowledge about other factors at this site, such as sedimentation rates and biological activity, to establish the cause of this change.

Site 9, which is closer to the Gordon River mouth than site 8, has much higher concentrations of copper at depth, although the surface concentrations are similar. The concentrations remain above the quality guideline values until about 24 cm depth. The iron and manganese profiles show a gradual decline with depth and are also higher than those at site 8. The particles at this site are mostly fines (< 63 μ m), so it seems likely that this is a controlling factor here too. Based on the observations reported in table 4.5, they are apparently from the Gordon River rather than the King River and therefore expected to be low in copper. The elevated sediment copper concentrations may occur because of adsorption of copper onto the fine particles or because of the formation of copper sulfide precipitates. However, it is not likely that they were transported here on sediment particles directly from the King River.

Site 10 showed very high concentrations of copper at the surface, comparable with those measured for the delta sites. Concentrations well above the sediment quality guidelines continue down to about 20 cm depth, after which they decrease to levels lower than the guidelines at about 30 cm. Again the particle size was predominantly <63 μ m. While there was evidence for the presence of material originating from the King River in the top sediment layers based on the physical examination of the sediment, the influence of the Gordon River material was still substantial as demonstrated by the presence of sulfide at this site. Therefore, the predominant mechanism of copper transport here is likely to be a combination of the mechanism operating for the northern and southern harbour sites. This could explain the very high copper concentrations observed.

4.2.3 Acid-volatile sulfide and simultaneously extracted metal measurements of the sediment

Data on AVS and SEM levels are given in table 4.6. The difference between the SEM and the AVS measurements indicate the potential toxicity of the sediments to benthic organisms (Batley 1995), with positive values (given in bold) predicting potentially toxic sediment. These measurements indicate that the King River sediment contains very little AVS (predominantly amorphous FcS). Other studies have shown that the tailings material has substantial amounts of pyrite (FcS₂), but have also indicated the presence of highly localised AVS on the delta (Taylor et al 1995). On the other hand, AVS phases are readily formed in sediment originating from the Gordon River. This has implications for the toxicity of sediments for various regions in the harbour.

Copper (50–75%) and zinc (10–30%) were the two main components of SEM, generally constituting over 85%. Lead was not measured, but its concentrations were estimated from those reported in Kochnken (1996) and are included in the SEM values in table 4.7. Lead was the next highest constituent, then chromium and nickel, which together were less than 5%. A notable exception to this was the deepest sediment core section at site 6, where copper was only 10% and zinc was 50%. This deep sediment may be representative of that before the tailings-derived material began depositing here, which is further evidence for site 6 being close to the limit of deposition of material from the King River.

Amongst the northern harbour sites (1–5) there is a general trend for the SEM levels to decrease with distance from the King River delta. This result implies that the form of the SEM, and thus the copper, changes with dispersal from the King River. This is shown in table 4.7 below. All of these sites, apart from site 5 at depth, have virtually no AVS and are therefore predicted to be toxic. The most toxic sediments, according to AVS/SEM theory are found at site 1 and in the surface layers of site 5. This implies that most of the sediment in the northern harbour is potentially toxic.

| Site | Depth | AVS | SEM | SEM-AVS ¹ |
|------|-------------|----------|----------|----------------------|
| | (cm) | (µmol/g) | (µmol/g) | (µmol/g) |
| 1 | 0 - 3 | <0.10 | 13.3 | 13.2 |
| | 3 - 6 | <0.10 | 15.0 | 14.9 |
| | 21 - 24 | 0.32 | 15.0 | 14.7 |
| 2 | 0 - 1.5 | 0.10 | 7.0 | 6.9 |
| | 1.5 - 4.5 | 0.11 | 11.1 | 11.0 |
| | 4.5 - 7.5 | 0.22 | 14.2 | 14.0 |
| | 28.5 - 31.5 | 0.12 | 9.2 | 9.1 |
| 3 | 0 - 3 | <0.10 | 6.2 | 6.1 |
| | 3 - 6 | <0.10 | 3.6 | 3.5 |
| | 18 – 21 | 0.18 | 6.2 | 6.0 |
| 4 | 0 – 3 | 0.46 | 6.8 | 6.3 |
| | 3 - 6 | <0.10 | 10.0 | 9.9 |
| | 24 – 27 | 0.11 | 12.1 | 12.0 |
| 5 | 0 – 1 | <0.10 | 2.0 | 1.9 |
| | 1 – 4 | <0.10 | 17.2 | 17.1 |
| | 4 – 7 | 0.11 | 15.6 | 15.5 |
| | 25 - 28 | 18.0 | 14.6 | -3.4 |
| 6 | 0 – 3 | <0.10 | 4.2 | 4.1 |
| | 3 - 6 | 11.3 | 11.3 | 0.0 |
| | 12 – 15 | 25.2 | 0.9 | -24.3 |
| 7 | 0 – 1 | 0.28 | 2.8 | 2.5 |
| | 1 – 4 | 5.2 | 3.4 | -1.8 |
| | 4 – 7 | 0.14 | 3.7 | 3.6 |
| | 22 – 25 | 11.4 | 2.2 | -9.2 |
| 8 | 0 – 1.5 | 16.4 | 2.6 | -13.8 |
| | 1.5 - 4.5 | 27.2 | 4.2 | -23.0 |
| | 4.5 - 7.5 | 21.1 | 3.5 | -17.6 |
| | 19.5 - 22.5 | 11.0 | 2.6 | -8.4 |
| 9 | 0 – 1.5 | 19.3 | 3.0 | -16.3 |
| | 1.5 – 4.5 | 142 | 8.9 | -133 |
| | 4.5 ~ 7.5 | 68 | 8.0 | -60 |
| | 19.5 - 22.5 | 30.7 | 4.8 | -25.9 |
| 10 | 0 – 3 | 20.6 | 11.6 | -9.0 |
| | 3 – 6 | 98 | 10.6 | -87 |
| | 18 – 21 | 45 | 11.6 | -33.3 |

Table 4.6 Acid-volatile sulfide (AVS) and simultaneously extracted metal (SEM) concentrations in sediment cores

1 Positive values (in bold) indicate potentially toxic sediment

The surface sediment at sites 6 and 7 have some potential for toxicity, but the AVS levels are higher at depth which would tend to bind up the metals. Both AVS and SEM levels are low at site 7, because of the sandy nature of the sediment. Very low SEM levels were found at site 8, but the AVS levels were substantial. Site 9 had SEM levels that were comparable to the delta sites, which is interesting, but also had very high AVS levels and is therefore predicted to be non-toxic. Site 10 had even higher SEM values but also had very high AVS values and is also predicted to be non-toxic. These results are similar to those reported by Koehnken (1996). This demonstrates that the origin of the sediment material is critical to its potential toxicity with the southern-most region of the harbour, despite having high metal concentrations, not predicted to be toxic to benthic organisms.

Table 4.7 shows the percentage of the total particulate copper that is acid leachable. This is important because the acid leachable fraction is another indicator of potential bioavailability, this fraction being more reactive. The proportion of acid leachable copper increases with

| Site | Depth | Total particulate copper | Acid leachable copper | acid leachable copper |
|------|-------------|--------------------------|-----------------------|-----------------------|
| | (cm) | (mg/g) | (mg/g) | (%) |
| 1 | 0 - 3 | 1.04 | 0.64 | 65 |
| | 3 - 6 | 1.12 | 0.66 | 64 |
| | 21 - 24 | 0.93 | 0.75 | 81 |
| 2 | 1.5 - 4.5 | 1.09 | 0.50 | 46 |
| | 4.5 - 7.5 | 1.13 | 0.46 | 41 |
| | 28.5 - 31.5 | 1.03 | 0.42 | 41 |
| 3 | 0 - 3 | 1.36 | 0.24 | 18 |
| | 3 - 6 | 1.16 | 0.13 | 12 |
| | 18 – 21 | 1.04 | 0.22 | 21 |
| 4 | 0 - 3 | 1.43 | 0.32 | 22 |
| | 3 - 6 | 1,46 | 0.47 | 32 |
| | 24 – 27 | 1.06 | 0.46 | 41 |
| 5 | 1 – 4 | 1.15 | 0.71 | 53 |
| | 4 - 7 | 1.07 | 0.65 | 56 |
| | 25 – 28 | 0.92 | 0.58 | 64 |
| 6 | 0 - 3 | 0.99 | 0.20 | 20 |
| | 3 - 6 | 0.72 | 0.56 | 78 |
| | 12 - 15 | 0.018 | 0.005 | 28 |
| 7 | 1 – 4 | 0.16 | 0.15 | 96 |
| | 4 - 7 | 0.18 | 0.17 | 97 |
| | 22 – 25 | 0.14 | 0.09 | 65 |
| 8 | 1.5 - 4.5 | 0.24 | 0.19 | 79 |
| | 4.5 - 7.5 | 0.14 | 0.15 | 110 |
| | 19.5 - 22.5 | 0.14 | 0.10 | 77 |
| 9 | 1.5 - 4.5 | 0.77 | 0.39 | 50 |
| | 4.5 - 7.5 | 0.60 | 0.35 | 59 |
| | 19.5 - 22.5 | 0.25 | 0.14 | 56 |
| 10 | 0 - 3 | 1.35 | 0.59 | 44 |
| | 3 - 6 | 1.30 | 0.51 | 39 |
| | 18 – 21 | 0.89 | 0.54 | 60 |

 Table 4.7 Comparison of total particulate copper and acid leachable copper from sediment cores at sites 1 to 10

distance from the delta. This is most probably due to the weathering of copper minerals (eg chalcopyrite) over time, given that surface sediments further from the delta are likely to be older. Sediment particle size is the main factor in the southern harbour sites. Sites 7 and 8 have the highest proportion of acid-leachable copper and the larger sediment particle sizes also. Site 7 has about 100% of the copper in this acid-leachable fraction in the surface sediments and also has the largest particle size. Sites 9 and 10 have predominantly $<63\mu$ m particles and have significantly lower percentages of acid-leachable copper. This probably reflects more rapid diagenetic processes in finer sediments, with non-acid leachable copper minerals forming more rapidly at site 9 and 10 due to the higher sulfide levels present.

4.3 Macquarie Harbour sediment pore waters

Profiles of dissolved copper, iron, manganese, silicon and potassium, obtained from duplicate peepers from sites 1 to 10, are shown in Appendix 3. Included here are pH profiles, which were measured in sediment cores obtained from each site, as these are indicative of pore water pH values.

Peepers were deployed so that in each case at least four or five chambers were exposed to the water column. However, one peeper at site 2, both at site 4 and one at site 8, were buried by the movement or deposition of sediment during equilibration. This was evident from all of

the elemental profiles obtained from these peepers and was fortuitous as it provided good examples of pore water profiles under various sediment conditions.

Several site types can be identified from these profiles including sites on the delta that do not appear to have had a recent deposition of sediment, sites on the delta that have undergone recent sedimentation, northern harbour sites that are significantly influenced by the King River, and southern sites that are influenced to a lesser extent by the King River. The peepers that conform to each description are given in table 4.8, along with their site locations. Those that were not buried were considered to represent the pore waters under 'stable' conditions, whereas the buried ones represented the pore water behaviour under the influence of large sediment movements, either due to resuspension events or slumping of the deltaic sediments. Each site type is discussed in turn below.

| Site types | Peeper label | Respective sites |
|--|---|-----------------------------------|
| 'Stable' delta sites | G, X, U (large) | 2, 3, 3 |
| Delta sites that experienced sediment burial | W, T, O | 2, 4, 4 |
| Northern harbour sites | K, J, D, T (large) | 1, 1, 5, 5 |
| Southern harbour sites | F, J (large), R, I (large), L, H, N, V, B, A | 6, 6, 7, 7, 8, 8, 9, 9, 10, 10 |

For the delta sites, the main differences between the 'stable' and 'buried' sediment were observed for the copper and iron profiles. Under the 'stable' conditions, the copper profiles showed well-defined maxima at the sediment-water interface (from about 0.2–0.5 mg/L). Within the limits of the resolution of the peepers, it seems probable that this maximum actually lies just below the interface. The profiles of iron and manganese generally indicated a redox boundary in the top few centimetres of sediment, but one that was not as well-defined as that commonly observed in other estuarine systems (Teasdale 1995 unpub). These profiles indicate that there is a release of copper at the sediment-water interface, which occurs under oxygenated conditions. The most probable explanation for this is the oxidation of copper-containing sulfidic minerals.

The profiles for the peepers in sediment that were recently buried offer a contrast in behaviour. For copper, there is a very large release in the top few centimetres of sediment, with the concentration decreasing with depth. Unfortunately, as these peepers were all buried, we do not have information on the profiles across the sediment-water interface. However, it seems highly likely that there would be a considerable flux into the overlying waters. The iron and manganese profiles also provide useful information. The manganese profile, which can be assumed to represent Mn^{2+} concentrations, indicates reducing conditions to the top of the peeper in all cases. The iron profile, on the other hand, suggests that oxidising conditions extended quite deep into the sediment, below the 5 cm depth and the redox boundary is not well-defined. This is not unexpected for sediment that is recently deposited and both profiles indicate that reducing conditions were beginning to establish, being at a transition level between the conditions where iron and manganese oxyhydroxides are reduced. These observation suggest a different mechanism is operating to that for the 'stable' sites, one which involves a change in redox conditions. Laboratory experiments are required to investigate the mechanism of copper release under both of these conditions.

Sites 1 and 5, the remaining northern harbour sites, are characterised by iron and manganese pore water concentrations that are an order of magnitude lower than for the delta sites that experienced sediment burial. The pore water copper concentrations, however, including the size of the maximum at the sediment-water interface are of the same order as those 'stable' sites on the delta. This implies that the same mechanism of release is operating. The profiles for site 5 are unusual in that they show quite regular peaks with depth for iron, manganese, silicon and copper concentrations. These could represent large sedimentation events in the past and also suggests that the sediment here is not vertically mixed to a significant extent.

Sites 6, 7 and 10 are characterised by an order of magnitude decrease in pore water iron concentration from that of the northern harbour sites. By contrast, manganese concentrations do not change significantly. The copper concentrations in the profiles at site 6 are generally lower than for the northern harbour sites, although with spikes that approach the higher levels seen there. The copper concentrations at sites 7 and 10 are lower still. One of the peepers at site 10 (peeper A) was reported by the divers to have been disturbed. The pore water profiles support this, as there is no indication of a redox boundary in the iron and manganese profiles until about 10-15 cm depth. The copper concentrations gradually increase to the overlying water levels from this depth also. By contrast, the other peeper from this site (peeper B) displayed a more distinct redox boundary at the sediment-water interface, and also the dissolved copper concentrations in the overlying water increased rather sharply above the sediment-water interface, indicating a flux of copper into the sediments. The peepers at site 7 also exhibit this behaviour. For site 6, however, the profiles are less clear cut, as they have copper concentration maxima near the sediment-water interface, more in keeping with that observed for the northern harbour sites. Therefore, although the metal pore water concentrations at this site are more similar to those found for the rest of the southern harbour sites, the direction of the flux across the sediment-water interface is not.

Sites 8 and 9 exhibit a further order of magnitude decrease in iron concentrations. The manganese concentrations at site 8 are also lower than the other southern sites. The copper concentrations are slightly lower but also exhibit a net flux of copper into the sediments, from the overlying waters.

The potassium and silicon concentration profiles are included as examples of non-redox dependant species and major ions, and are typical of those found in estuarine systems (Teasdale 1995, unpub).

The observations at all sites can be explained by the presence or absence of sulfide in the sediment. There is a definite relationship between the low pore water metal concentration (table 4.9) and the presence of sulfide in the sediments (table 4.6). As sulfide forms insoluble salts with all heavy metals, and very strongly with copper, the pore water concentrations of the metals will be low in the presence of high sulfide concentrations. This continual removal of metals from the pore waters means that the flux into the sediment pore waters will also continue. Thus, sulfidic sediments act as a sink for heavy metals, including copper, as long as they remain anoxic. If they should become oxygenated however there is potential for large scale copper release.

Table 4.9 summarises the data for the copper concentrations for the overlying waters, the maxima in the oxic pore waters and typical values for the anoxic pore waters for each site. These results demonstrate that those sites near the delta have pore water copper concentrations in the surface sediments far greater than both the overlying water concentrations and the deeper anoxic pore waters. In fact sites 1 to 6 all had surface pore

| Site | Overlying water ^{1, 2} (µg/L) | Maximum oxic zone ² (µg/L) | Median anoxic zone ² (µg/L.) |
|------|---|--|--|
| 1 | 47, 54 (17) | 64, 255 | 10, 14 |
| 2 | 32 (99) | 236, 4350 | 13, 25 |
| 3 | 37, 38 (26) | 120, 520 | 8.3, 16 |
| 4 | (34) | 1880, 3850 | 99, 114 |
| 5 | 20, 18 (13) | 84, 51 | 6.5, 8 |
| 6 | 14 (8.5) | 46 | 5.5 |
| 7 | 14 (10.8) | 5.1 | 2.1 |
| 8 | 4.5 (4.7) | 2.4 | 1.2 |
| 9 | 10, 11 (4.0) | 4.6, 7.4 | 0.9, 1.7 |
| 10 | 16 (5.0) | 3.3 | 1.6 |

Table 4.9 Summary of copper concentrations (μ g/L) in pore water and overlying water from peeper samples

1 values in brackets are from corresponding overlying water grab samples (1 m above the sediment-water interface)

2 two values at a site indicate replicate peepers

water copper concentrations greater than the overlying water concentrations, indicating that there was a flux into the overlying water for the copper as well as deeper into the sediment pore waters. At sites 7 to 10, on the other hand, the overlying water concentrations are greater, confirming a flux into the sediment pore waters only. Flux calculations based upon the peeper profiles at each site are shown in table 4.10 and discussed in section 4.5.

Therefore, it is apparent that sediment that produces sulfide, which can be considered to be of Gordon River origin, is a sink for dissolved copper from the overlying waters. By contrast, sediment that is dominated by King River material, which is very low in AVS and high in copper, is a source of dissolved copper for the overlying water. Based on the sediment characterisation results presented here, and in other studies, most of the northern harbour sediment appears to be of King River origin, while most of the southern harbour sediment appear to have originated from the Gordon River.

4.4 Collection of sediment species mobilised by oxidation

The use of plastic strip collectors to study the effect of oxygen introduction into estuarine sediment and pore waters has only recently been described (Allen et al 1995). There have been only limited field applications and their use in this study of Macquarie Harbour sediments was viewed as exploratory. Plots of the masses of deposited iron and copper, and copper to iron ratios, are shown in Appendix 4. Manganese was not included because the concentrations were much lower than for iron, and previous experience (Allen et al 1995) indicates that collected iron is more important, because the kinetics of iron oxidation are more rapid than for manganese. In many instances the stackers containing the strips became buried, so the sediment-water boundary was not always discernible. For these stackers, the y-axis represents a strip number rather than a depth.

The formation of a deposit on Lexan requires that iron be present in a reduced form, usually soluble, that deposits onto the surface when oxidised by oxygen diffusing out of the plastic. Copper and other metals in high concentrations in the immediately surrounding waters will also co-deposit to some extent. The deposition of copper will therefore require the presence of depositing iron, unless it can be independently released and precipitated by oxidation of sedimentary material.

The reason this method is inherently different to the water sampling methods, such as peepers, is that the deposition reactions are determined by the release of oxygen from the plastic, as well as the presence of oxygen from other sources, and the presence of any reduction processes. The latter will tend to counter deposition onto the material. It was believed that the use of Lexan collectors mimics the release and subsequent deposition of metals caused by burrowing organisms, which introduce oxygen at depth into anoxic zones.

The results in Appendix 4 demonstrate that there is a wide range of deposition patterns, particularly for iron. Iron deposits that are over about 100 μ g/strip, for most of the strips, were observed for the stackers from sites 1 and 6. Low iron deposits, less than 25 μ g/strip, were found at sites 8 and 9. All other sites (2, 3, 4, 5, 7 and 10) had predominantly intermediate values from 25–100 μ g/strip. These designations of high and low values are arbitrary and serve only as a convenient means to differentiate the observations. Comparing these results with the high and low iron concentrations in the pore waters indicates a good correlation for the sites with low pore water iron (sites 8 and 9), but a poor correlation for the sites with higher iron concentrations (sites 2, 3 and 4).

The results for the deposited copper concentrations were less variable. They could only reasonably be split into two groups, those with high copper deposits (>0.2 μ g/strip), which were sites 1 to 7. Sites 8, 9 and 10 had copper deposits generally less than 0.2 μ g/strip. The correlation between these results and the pore water copper concentrations is marginally better than for iron. These results indicate that a fraction of the copper in the sediment is mobilised when exposed to oxygen, as would occur in the presence of benthic organisms.

An interesting way of looking at the data is to use the copper to iron ratio, given the probable dependence of copper upon the precipitation of iron. Using a comparison between the 'regularity' of the copper and iron depth profiles and the ratio plot as an indication of covariance, it is apparent that for sites 1 to 6 the ratio represents a real trend more so than either of the metal profiles. This indicates that the copper is likely to be coprecipitating with the iron at these sites. Sites 8 and 9, on the other hand, have much more regular plots for the copper and iron profiles than for the ratio plot, which is quite scattered. This suggests that the copper deposition here is not due to coprecipitation with the iron, but may be due to oxidation of a copper sediment species. Sites 7 and 10 have elemental and ratio profiles of comparable regularity, indicating a possible intermediate condition. The influence of both King and Gordon River sediment would explain this observation at site 10 and the coarse sandy sediment at site 7 would produce different conditions also.

The most likely explanation for these observations is, once again, the presence or absence of sulfide within the sediment. There is very little reactive sulfide (AVS) in the northern harbour sites, which means that the deposited iron is probably from reduced pore water iron. Copper will therefore coprecipitate as described above, and thus the elemental profiles are scattered but the ratios indicate a trend. By contrast, the phase being oxidised in the southern harbour sediment, where there is abundant reactive sulfide, is probably amorphous $CuS_{(s)}$. Likewise, the form of iron being oxidised is amorphous $FeS_{(s)}$. Thus the iron and copper profiles indicate possible trends, whereas the ratio plot is quite scattered, indicating poor interdependence between the mobilisation of each metal.

Furthermore, the dynamic nature of the method is such that under strongly reducing conditions, such as arise in sulfidic sediments, the oxyhydroxides and associated trace metals initially deposited will be removed. Thus lower concentrations of iron and copper were collected at the sites with high sulfide levels. This observation may be somewhat misleading with regard to the amount of copper released initially, because of the long sampling time

involved here and the opportunity for sulfidic conditions to re-establish around the stackers. It is possible that the initial copper deposition under these conditions is greater than for the northern harbour sites. A time series study involving retrieval of stackers over this time period, would be required to investigate this possibility thoroughly.

4.5 Determination of benthic and sedimentation copper fluxes in Macquarie Harbour

4.5.1 Benthic copper fluxes from peeper pore water profiles

From the profiles of dissolved copper in the sediment pore waters, obtained with the pcepers, the flux (amount of material transferred per unit area per unit time) of copper into the overlying water, or into the sediments, may be calculated. We assume that the transfer is purely by diffusion; a reasonable assumption for much of the harbour given the paucity of benthic macro organisms. Following Berner (1980) the relationship between the flux (F) and the sediment concentration gradient is given by:

$$\mathbf{F} = -\mathbf{D}_{s} * \frac{\partial \mathbf{c}}{\partial z} \big|_{z=0}$$

where F is the flux, D_s is the diffusion coefficient of copper in the sediment, and the partial differential is the concentration gradient at the sediment-water interface.

The sediment diffusion coefficient (D_s) was not measured, but was inferred from the porosity (ϕ) of the sediment surface layer (assumed to be 0.9, Li & Gregory 1974) and the diffusion coefficient (*D*) of copper ion in seawater (5.88 x 10⁻⁶ cm² /s, Li & Gregory 1974) by the relationship:

$$D_s = \phi * D$$
 10

The peeper concentration data provides a good estimate of the concentration gradient at the interface. Table 4.10 shows the calculated fluxes of copper into the water column from the sediment. It is apparent that the deltaic sediments (sites 2–4) produce a very large flux of copper into the overlying waters although there is considerable spatial heterogeneity. This could be due to the presence of at least two different mechanisms of copper release from these sediments, as is discussed in section 4.3. The other sites that have a flux of dissolved copper into the overlying waters are sites 1, 5 and 6, where sediment of King River origin has been deposited. Sites 7–10 all show small fluxes of copper into the pore waters, indicating removal of copper from the overlying waters.

4.5.2 Benthic copper fluxes from benthic chamber deployments

Due to the problems experienced with the sampling equipment on the second field trip, which meant that the samples were not able to be filtered until several weeks later, of the metals analysed in samples collected from the benthic chambers, only manganese showed a systematic increase with time in both filtered and unfiltered samples. This is probably because of the slow kinetics of manganese oxidation, whereas dissolved iron had probably been oxidised and precipitated out well before the sample could be filtered. This would have affected the partitioning between the particulate and dissolved fractions of most heavy metals and made it difficult to determine the change in dissolved concentrations during the deployment. Thus benthic fluxes could not be calculated directly.

| Site | Peeper | Cu concentration gradient | Calculated flux of Cu ¹ |
|------|-----------|---------------------------|------------------------------------|
| | | (mg/L/cm) | (kg/km²/yr) |
| 1 | J | 0.05 | 100 |
| | к | 0.08 | 148 |
| 2 | G | 0.13 | 247 |
| | W | 2.2 ² | 4080 |
| 3 | U (large) | 0.40 | 740 |
| | X | 0.17 | 310 |
| 4 | 0 | 1.4 ² | 2600 |
| | Т | 3.4 ² | 6300 |
| 5 | D | 0.08 | 148 |
| | T (large) | 0.04 | 74 |
| 6 | F | 0.05 | 92 |
| | J (large) | 0.025 | 46 |
| 7 | R | -0.006 | -11 |
| | l (large) | -0.005 | -9 |
| 8 | L | -0.04 | -74 |
| | н | -0.035 | -65 |
| 9 | N | -0.003 | -5 |
| | V | -0.002 | -4 |
| 10 | А | -0.003 | -6 |
| | в | -0.005 | -9 |

Table 4.10 Calculation of copper fluxes across the sediment-water interface

1 positive values (in bold) indicate a net flux from the sediment into the overlying water, negative values indicate a flux into the sediments

2 as the profiles did not extend across the sediment-water interface for these peepers, the concentration gradients were estimated using the copper concentration maxima in the oxic surface sediment and the dissolved copper concentration from the grab samples (Table 3.9)

An attempt was made to infer the copper flux rates from the manganese rates. The rationale was that in several cases the slope of the concentration vs depth profile for pore water copper and manganese concentrations (obtained from the peepers), as well as their absolute magnitude, were very similar. However, it was decided that this was not a valid procedure and also not necessary due to the success of the peeper deployments.

4.5.3 Sedimentation fluxes from sediment trap deployments

Data obtained from sediment trap deployments at a limited number of stations (table 4.11), provide a further insight into processes involving copper, iron and manganese in the waters and sediments of Macquarie Harbour. Several generalisations emerge from the data:

- Particulate copper concentrations at sites 2, 3, and 5 in the King River delta, were significantly higher (p=0.01) than at other sites and were virtually identical. The absolute amounts of material sedimenting here were also the highest of all sites.
- The mass flux of material at the northern harbour sites were greater than for the southern harbour sites
- The sites with high fluxes of dissolved copper and high sedimentation rates also had high iron to manganese ratios. In contrast sites in the southern harbour, with lower fluxes of sedimenting copper, had low iron to manganese ratios.

From the sediment trap data (total mass and copper concentration), the mass flux of copper contained in particles sedimenting from the water column to the sediment could be calculated. An implicit assumption in the following discussion is that this does not originate from resuspension and deposition of already settled material. This assumption may not be valid for the sites close to the delta where resuspension of the delta deposits by storm events is possible. Bearing this caveat in mind, the results in table 4.12 show that the delta sites are sinks of particulate copper. The deposition rates at the sites remote from the delta are about an order of magnitude smaller, but these sites are also sinks of particulate copper.

| Table 4.11 | Mass flux of sediment from |
|--------------|----------------------------|
| sediment tra | ap measurements |

| Site | Total sedimentation flux |
|------|--------------------------|
| | (kg/km²/y) |
| 2 | 1 200 000 ¹ |
| 3 | 530 000 |
| 5 | 980 000 |
| 11 | 108 000 |
| 12 | 185 000 |
| 10 | 224 000 |

| Table 4.12 | Flux of copper in particulate |
|-------------|-------------------------------|
| material se | ttling to the sediments |

| Site | Sedimentation copper flux ¹ (kg/km²/y) |
|------|--|
| 2 | 3660 |
| 3 | 1740 |
| 5 | 2800 |
| 11 | 244 |
| 12 | 277 |
| 10 | 480 |

1 estimated from the information in table 3.12 and assuming that the copper concentrations were similar for sites 3 and 5 1 a positive flux here is from the overlying water into the sediment

The change in the iron to manganese ratio, between the northern and southern harbour sites, probably reflects the different rate at which these elements oxidise, coagulate and sediment out of the water column. The overlying water measurements indicated that the proportion of dissolved and particulate forms of iron changed in the surface waters between the northern and southern harbour water. Much of the iron sedimented out in the northern harbour area.

4.5.4 Mass balance of copper in Macquarie Harbour

If we assume that the average of the fluxes of dissolved copper measured at sites 2, 3 and 4, apply to the whole area (15 km^2) bounded by the landward side of the delta and a north-south line running from the eastern bank of Long Bay, and an east-west line from Connelly's Point, then the flux of dissolved copper into the water is 35 700 kg/y. From table 4.12, the flux of copper contained in the particles settling out in the same area is 46 000 kg/y. Therefore despite the large flux of dissolved copper out of the sediments, there is a net flux of total copper into the delta sediments. This means, more copper is removed from the water column as particulate than enters the water column in dissolved form. However, these fluxes are of a similar magnitude and it is possible that, under some conditions, the net flux of total copper will be into the overlying water at the delta.

If we consider that the removal of particulate copper in the remaining 250 km^2 of the harbour is approximated by the mean value of the bottom three entries in table 4.12, then the flux of copper contained in the sedimenting particles is $850\ 000\ \text{kg/y}$. The contribution of the dissolved fluxes in this region, generally being less significant, can be disregarded for our purposes here. This sets a lower limit to the additional inputs from the King River of 95 000 kg/y.

This value is a lower limit and could be considerably greater as the losses due to tidal exchange have been ignored. The availability of hydrographic data, specifically the volume of water entering and leaving the harbour, together with concentrations of dissolved and particulate copper would pin this value down and provide a useful crosscheck on calculation of the River inputs from direct measurements of the river copper concentrations and flow rates. Estimates based on monitoring in the King River are 7–30 times the above lower bound (L Koehnken pers. comm.).

5 Preliminary model of copper cycling in Macquarie Harbour

Based on the information obtained from this study a preliminary model of copper cycling in Macquarie Harbour is proposed (figures 5.1-5.3). Three zones of cycling, which are characterised by different dominant geochemical processes and different copper fluxes across the sediment-water interface, are identified as part of this model. Figure 2.3 indicates regions of the harbour that correspond to each of the zones described here.

5.1 The King River delta

The King River transports copper (figure 5.1) in three forms to the delta region:

- Particulate copper (pCu) which includes a mixture of copper ore particles and copper adsorbed onto other materials (Mount Lyell Remediation Research and Demonstration Program Project 5). The latter form is in equilibrium with the dissolved copper with the equilibrium state depending largely upon the pH of the river water.
- Colloidal copper (cCu) which is possibly the major form of copper in the King River. The colloidal material will predominantly be iron and manganese oxyhydroxides and the copper will have adsorbed onto these materials or have coprecipitated with them. Results from Koehnken (1996) suggest that the copper is associated most strongly with manganese colloidal forms. These will also be in equilibrium with the dissolved copper and dependent upon pH.
- Dissolved copper (dCu) which will be present predominantly as inorganic species. At low pH levels this could constitute the major form of copper in the river (Mount Lyell Remediation Research and Demonstration Program Project 14).

When these waters mix with the saline Macquarie Harbour waters, at about 1-5%, the colloidal forms may coagulate and either form particle-sized material or coat onto such material already present. The saline waters will also act to neutralise the river water and increase the pH levels which may cause additional adsorption of dissolved copper onto the



Figure 5.1 Preliminary model of copper cycling in the King River delta

particles present and forming. It will also cause oxidation and precipitation of iron and manganese to occur more rapidly (particularly the former). The oxidised iron will form new colloids and particles and at this point the iron and copper chemistry become more closely linked. The processes in the mixing zone are very complex and need to be studied specifically to determine the exact changes occurring. Larger particulate material will sediment out, adding copper to the delta sediments. Smaller particulate, colloidal and dissolved forms will be transported to the surrounding Macquarie Harbour waters.

The delta sediment is dynamic and probably undergoes frequent slumping or resuspension in certain areas. These events produce very high pore water concentrations and therefore are expected to produce a large flux of copper into the overlying water. Other more stable regions of the delta experience a smaller scale release of copper into the sediment pore waters. This also produces a diffusive flux into the overlying waters, although not as large as the one observed for the above phenomenon, and also a flux into deeper sediment where the pore water concentrations are probably controlled by adsorption. The exact nature of these copper-releasing mechanisms are unknown but they seem linked to redox processes. The relative areas of sediment that experience these processes is very important for the total fluxes of copper that enter the water. Based on the observed burial of some peepers deployed in this area, it may be as much as half of the delta region that experiences this large release. The copper released into the overlying water will experience the same processes as that from the King River. Some of it will probably readsorb onto sedimenting and forming particles and the rest of it can be transported around the harbour in the bottom water layer, where concentrations are determined by dilution with the saline harbour waters.

5.2 Northern Macquarie Harbour

The copper inputs into the northern Macquarie Harbour (figure 5.2) include all the forms leaving the delta zone as well as the dissolved and colloidal copper being transported back from the southern harbour. This zone represents a limit to the dispersal of particulate matter direct from King River inputs, of which only smaller particles sizes remain. These particles sediment out and are buried as on the delta site. Further coagulation and sedimentation of colloidal material may occur, particularly at the interface between the low salinity surface waters and the high salinity bottom waters. These processes also produce a flux of particulate copper into the sediment. In this zone dissolved organic carbon (DOC) is present in significant concentrations, mostly in the surface waters, and may complex copper that is adsorbed onto particulate and colloidal material, as well as free dissolved copper. In general this mechanism will act to increase the copper levels (and other metals) in the dissolved fraction of which a significant proportion is likely to be bioavailable to organisms due to the complexation capacity being exceeded.

The sediment in this zone is similar in composition to that of the delta (at least at the surface), although it is much more stable and generally in deeper water. The major sedimentation events that caused the peepers to be buried are not as likely to occur in this zone and no consequent massive copper releases are therefore anticipated. However, the smaller scale release of copper, due to dissolution processes within the sediment, does occur here, as in the delta sediments and produces a dissolved copper flux into the overlying waters. Although this flux is smaller in magnitude than that observed on the delta, the area of this sediment is much larger and therefore this could be a significant source. However, much of this copper released would be adsorbed onto the sedimenting material and returned to the sediment. Consequently, the net flux at this zone appears to be into the sediment and the

main transport of copper out of this zone is in the <0.45 μ m filtered fraction of the surface and bottom waters (dCu and cCu). Although the surface waters have higher copper levels, the bottom waters are of much greater volume and therefore may represent the greater flux compartment.

Some areas in this zone will have fairly thin layers of sediment of this nature, overlying sediment that is typical of the southern harbour zone, and which has been proposed to represent the predominant sediment found in Macquarie Harbour before the tailings material began to deposit there. Site 6 is an example of such an area. These sites are interesting because they exhibit behaviour and conditions that are typical of what we have classified as, northern harbour sites for some parameters, and southern harbour sites for others. Given the importance of benthic copper fluxes into the overlying water, which occur at site 6, it was decided that it was typical of the 'northern' harbour zone. The presence of such sites also indicate that the range of deposition of tailings material has possibly been extended recently. This could be due to the effects of the power station on the discharge of the King River.



Figure 5.2 Preliminary model of copper cycling in the northern Macquarie Harbour

5.3 Southern Macquarie Harbour

The main copper inputs into this zone (figure 5.3) are the dissolved and colloidal forms transported from the northern harbour zone. We propose that the transport of particulate copper, originating in the King River, to this zone occurs infrequently. The major water inputs into this zone are the Gordon River for the surface waters and the Southern Ocean for the bottom waters. Both have lower dissolved copper levels than the Macquarie Harbour waters and thus act to dilute the copper concentrations. In addition, the Gordon River is a major source of the DOC for the harbour.

The water column interactions are similar to those in the northern harbour zone except that any sedimenting material is predominantly formed by precipitation and coagulation of dissolved and colloidal forms (predominantly iron and manganese). Dissolved copper species can adsorb onto these particles and there is once again a flux of particulate copper into the sediments. Dissolved and colloidal copper in the surface waters that are not scavenged in this manner can be transported back into the northern harbour zone in the surface waters, mainly through mixing with the Gordon River inflow.

The bottom waters, on the other hand, experience different conditions. The sediment in the southern harbour zone has reactive sulfide (AVS) present. This has two important effects. Firstly, the sediment is strongly reducing instead of mildly reducing, as in the northern and delta sites. This means that the pore water maxima produced by oxidative processes in the surface sediments is not observed here. Secondly, any dissolved or reactive copper reaching the sediments will be precipitated as CuS. This means that the pore water concentrations are very low and thus there is a net flux of dissolved copper into the pore waters. The role of benthic organisms in this sediment is also important because they may produce a flux into the water column, by oxygenating the anoxic sediments. However, it is considered unlikely that this be more significant than the two fluxes described above. Overall, the southern harbour zone is a sink for copper in the harbour.

The area of the southern and northern harbour zones are about the same in the map shown in figure 2.3. This is an estimate based on the observations made in this and other studies. A more comprehensive examination of the harbour sediments is required in order to produce a more accurate estimate. It should be noted that some areas of sediment will not conform to the zone types described here. These will be the sandy sediment regions. Site 7 in this study may be representative of these sediments. If this is so, they will play a minimal part in the cycling of copper in Macquarie Harbour.



Figure 5.3 Preliminary model of copper cycling in the southern Macquarie Harbour

6 Remediation options for Mount Lyell tailing deposits in Macquarie Harbour

The results of our investigation of the physics and chemistry of the sediment and water in Macquarie Harbour, enables an assessment to be made of proposed tailings remediation options. From the point at which mine tailings enter the King River, to Macquarie Harbour, the river waters generally possess a low pH and as a consequence, high dissolved copper and iron concentrations. Along the banks of the river, mine tailings have accumulated, to the greatest extent near the delta at the mouth of the King. These exposed tailings are subject to oxidation and acidification with consequent copper and iron dissolution.

The important conclusions from Project 5 were that the principal source of copper to the river is the mine rather than the deposited tailings. Our mass balance calculations confirm that the King River is the source of at least 75% of the total copper entering the harbour. The first action therefore must be to stop this discharge and to then address the question of tailings deposits progressively down the river system, ending with the delta.

It is evident that, in the delta region, tailings that are buried by seawater are less of an environmental problem. However, there is a flux of dissolved copper out of the sediments, which we estimate to represent about 25% of the copper entering the harbour waters, so is a significant source. This is currently balanced by a flux of copper in particulate matter to the delta sediments, so the delta is not a net source of copper into the harbour. It is not possible to establish at this stage whether this will change as a result of terminating discharges from the Mount Lyell mine, the King River iron load is also decreased. A lot of this iron load precipitates out in the mixing zone over the delta, which may be the main process that scavenges copper from the water column. It is possible that the delta will become a net source of copper and iron to the harbour if this process no longer occurs to the same extent.

In the delta region, we observed instances where our pore water samplers were buried, during the period of deployment, by additional tailings material moved by wave action or river flow. It was typical for the surface pore waters in these samplers to have considerably greater dissolved copper concentrations, and we believe this is related to differences in the surface chemistry of freshly input tailings material, and the time taken for reducing conditions to establish. The redox boundary as defined by the dissolved iron concentration in these cases is deeper in the sediment than in the unburied peepers. It raises the concern that the copper fluxes from newly dumped sediments are likely to be high. Furthermore, our measurements of acid-volatile sulfides show that the delta sediments are very low compared to sediments in the southern harbour, and have a lesser capacity to immobilise copper once it is in the sediments. For these reasons, remediation of the tailings material present in the delta needs to be considered.

Another important consideration is that the copper complexation capacity seems to have been exceeded already in most of the harbour waters. Therefore, any release of dissolved copper is likely to be largely bioavailable until it is scavenged by other processes. A discussion of the likely impact of proposed remediation relevant to copper cycling in Macquarie Harbour is given below.

6.1 Delta remediation options

6.1.1 No action

Even if the upstream sources of copper (which are the major ones) are remediated, the delta will continue to be a significant source of copper to the harbour waters. The flux estimates from this

study should be compared to riverine flux estimates arising from the other projects. Modelling studies are required to predict copper concentrations in the harbour under this scenario.

6.1.1 Partial delta revegetation

One possible beneficial side effect of revegetation will be an increase in the organic material in the delta sediments which may enable sulfide producing bacteria to establish on the delta. This will act to immobilise the sediment copper (see *in situ* tailings treatment discussion). The potential harmful effects of copper in terrestrial foodchains will need to be considered here however.

6.1.3 Dredging options (tailings removal, channel dredging, lowering the delta etc)

Any dredging operation will cause a temporary increase in the dissolved and particulate copper load around the harbour. The size of this release is likely to be proportional to the scale of the dredging operation. The effect of this pulse on biota is difficult to estimate but it could result in acute toxicity, with consequences that last longer than the pulse. Laboratory modelling studies are required to quantify copper release during dredging.

6.1.4 Capping the delta

This will require a minimal amount of dredging to lower the delta which will produce an initial pulse of copper release, but can then be combined with partial revegetation of the delta.

6.1.5 King River diversion

The delta will continue to be a source of dissolved copper even if the King River is diverted. The lack of material from the King River inputs that performs a scavenging function may act to increase the net copper fluxes into the harbour from the delta.

6.2 Tailings remediation options

6.2.1 Relocation of tailings within harbour

Our studies indicate that this is likely to produce a large release of copper upon the initial deposition (and also from the dredging, see above) and then a continued gradual release of copper from the sediment into the overlying water, unless it is relocated to the southern end of the harbour, where the copper will be immobilised by precipitation as sulfides. However, the latter option is also likely to be unacceptable on the grounds of conservation and public relations. This release may also produce acute toxicity to organisms.

6.2.2 In situ tailings treatment

More information on possible options is required before specific comments can be made. However, based on the results of this investigation, any option that increases the reactive sulfide concentration of the delta will act to immobilise the copper provided that the sediment is not exposed to air, otherwise acid mine drainage will still occur.

7 Recommendations for future work

In the course of these studies, a number of knowledge gaps were identified, where additional information would add considerably to the reliability of our conclusions and would ultimately provide a more sound basis for dediding management options for remediation anfd rehabilitation. It is possible that some of these issues have been covered elsewhere in the Program.

1. Further examination of the copper release mechanisms from the tailings-derived sediment, under stable conditions and conditions of large sediment deposition. This should include detailed field characterisation of the sediment transport and deposition

processes occurring around the delta, and consideration of temporal effects. Laboratory experiments investigating copper release from the sediment particles under various redox conditions should be carried out.

- 2. Investigation of acid-volatile sulfide, particulate and pore water copper concentrations in deep water sediments and also along the western shore of Macquarie Harbour to allow a better understanding of the distribution of sediment zones (as discussed in section 5.3) within the harbour.
- 3. High resolution spatial and temporal studies of redox conditions in the water column and sediment at each of the harbour zones identified, as the mobilisation and immobilisation processes are closely linked to redox changes.
- 4. A more detailed examination of the water circulation patterns and the resulting particulate transport behaviour. This should be linked with the more extensive investigation of sediments to establish the limit of deposition of King River material and whether this has changed over time.
- 5. Investigation of colloidally-mediated processes including transport, coagulation and settling. Attention should be given to the changing role of manganese and iron colloids in transporting and depositing copper around the harbour.
- 6. A more detailed examination of the relationship between water column copper concentration (dissolved and particulate) and salinity, to establish the importance of removal processes versus theoretical dilution in various water layers. The role of complexation capacity in the various water layers should also be examined.
- 7. A more detailed examination of the forms of copper present in the sediment in the various zones of the harbour, focussing on their stability versus reactivity and how this changes with location.
- 8. A re-examination of the project findings following the availability of data from other projects. In particular the information should allow a more comprehensive analysis of the mass-balance of copper in the harbour.

8 Summary

Elevated concentrations of dissolved copper were measured throughout Macquarie Harbour. The highest dissolved copper concentrations were measured in the delta waters (up to 560 μ g/L). Elsewhere, surface water copper concentrations ranged from about 100 μ g/L in the north to 12 μ g/L in the south. Bottom water concentrations ranged from about 30 μ g/L on the delta to 4 μ g/L in the south. Dissolved copper concentrations were determined largely by dilution of King River water with seawater low in copper and flocculation processes occurring in the 1–5‰ salinity zonc. About 65–85% of the copper at all sites was in the <0.45 μ m fraction. Size fractionation studies suggest about 50–80% of the dissolved copper fraction was present in colloidal form in some northern surface waters. Dissolved copper correlated highly with dissolved manganese concentrations (r² = 0.97), suggesting that dissolved copper is largely associated with colloids high in manganese (probably combined with iron) in the harbour. The copper complexation capacity of dissolved organic matter was exceeded in most harbour waters and a significant proportion of the dissolved copper was present in an inorganic form which may be bioavailable.

Particulate copper concentrations in sediment from all sites, except site 7, exceeded sediment quality guideline criteria formulated overseas, reaching over 1300 mg/kg at some sites. High

particulate copper concentrations result from the deposition of copper-laden tailings material in the northern harbour and the coagulation of colloidal copper and its deposition in the southern harbour. Copper was effectively immobilised in the southern harbour sediments by the presence of high levels of reactive sulfide which forms insoluble precipitates with copper. Acid-volatile sulfide measurements predicted low sediment toxicity at the southern harbour sites, whereas the toxicity of sediments from the northern harbour sites were predicted to be potentially high as a consequence of the low sulfide levels. A significant fraction of copper in the sediment was acid leachable (15–80%), which is another measure of potential bioavailability. This fraction increased with distance from the delta which is probably a reflection of weathering and oxidation of sulfide minerals.

Pore water copper concentrations measured on the delta were as high as 4000 μ g/L in locations that experienced recent sediment deposition. This has serious implications for proposed dredging activities on the tailings material. At the more stable regions of the delta, and for the rest of the northern harbour region where tailings material had been deposited, pore water copper concentrations were in the order of 50–500 μ g/L. Based on the pore water copper profiles, a flux of about 35 700 kg/y of dissolved copper from the sediment to the overlying water was calculated for the delta region. The pore water copper concentrations in the south were less than 8 μ g/L at the surface sediments and decreased to less than 2 μ g/L at depth. The low copper concentrations are a result of high sulfide concentrations which control the solubility of copper in the sediments and maintains a dissolved copper flux into the sediment.

Fluxes of copper in sedimenting particles, which also act to remove copper from the water column, were calculated to be 46 000 kg/y on the delta. This is slightly greater than the flux of dissolved copper out of the sediments, thereby making the delta a net sink of copper under the conditions experienced during this study. The flux of particulate copper from the water column into the sediment for the rest of the harbour was about 85 000 kg/y. A mass balance calculation indicated that copper inputs for the King River were at least 95 000 kg/y, making it the source of 75% of the copper into the harbour waters. It must be stressed that the mass balance calculations presented in this work represent only a snapshot of the system and do not take into account temporal variations in copper transport or cycling.

A preliminary conceptual model of copper cycling in Macquarie Harbour has been proposed. Based on the nature of the sediment and the measured copper fluxes, there are three distinct zones. In the King River delta zone there are significant fluxes of dissolved copper from the sediments to the water column. The northern harbour zone is characterised by a lower flux of copper but is a geographically larger area. The southern harbour zone however, acts as a sink for dissolved copper as a consequence of the sulfide-rich surface sediments. This model provides the basis for recommendations made regarding future work requirements and proposed remediation options. Appendixes

Appendix 1 Profiles of temperature, pH, salinity, dissolved oxygen, redox potential and turbidity in Macquarie Harbour waters at sites 1 to 10



SITE 1










SITE 5













Appendix 2 Particulate iron, manganese and copper in sediment cores from sites 1 to 10. Note concentrations are in mg/g, for ease of graphing

















SITE 6













SITE 10

Appendix 3 Depth profiles of iron, manganese, copper, potassium and silicon from pore water peeper measurements and pore water pH from sediment cores at sites 1 to 10

















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Sediment core


















































































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