

## 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

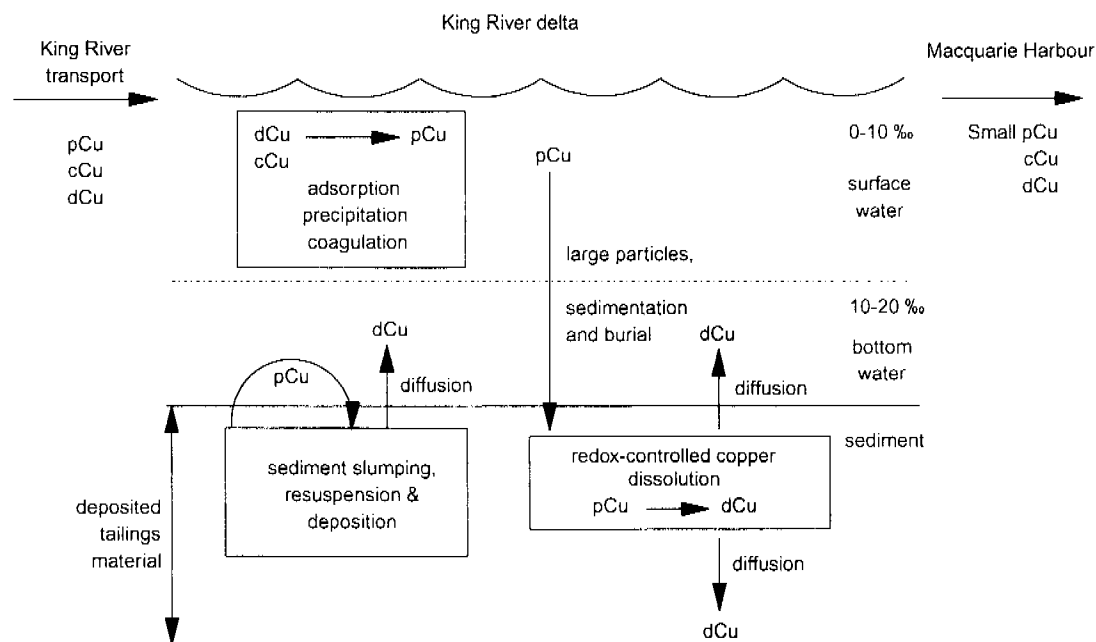


Figure 5.1 Preliminary model of copper cycling in the King River delta

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 re-adsorb 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  $<0.45 \mu\text{m}$  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.

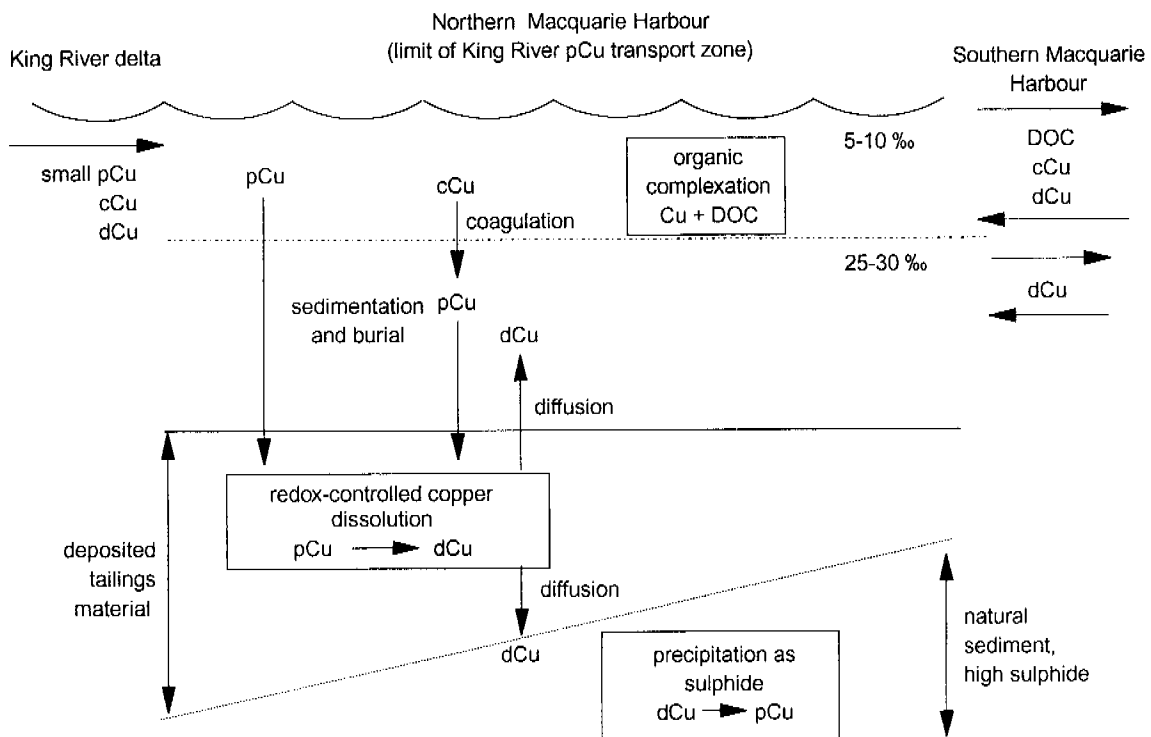


Figure 5.2 Preliminary model of copper cycling in the northern Macquarie Harbour

### 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.

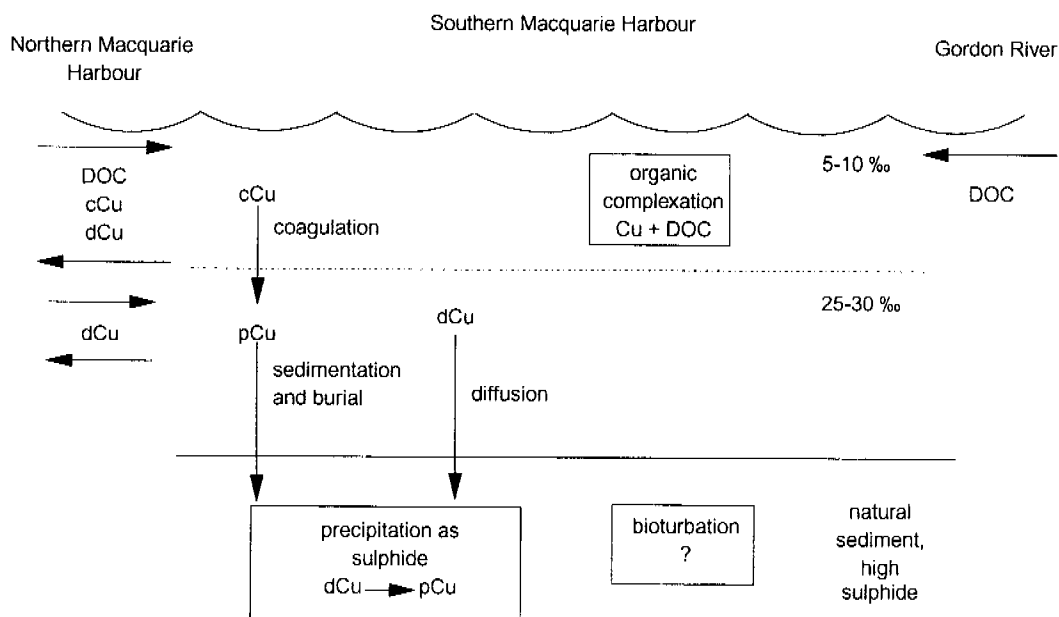


Figure 5.3 Preliminary model of copper cycling in the southern Macquarie Harbour

## **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 deciding management options for remediation and 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 colloiddally-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 µg/L). Elsewhere, surface water copper concentrations ranged from about 100 µg/L in the north to 12 µg/L in the south. Bottom water concentrations ranged from about 30 µg/L on the delta to 4 µg/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 zone. About 65–85% of the copper at all sites was in the <0.45 µm 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 ( $r^2 = 0.97$ ), 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 µg/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 µg/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 µg/L at the surface sediments and decreased to less than 2 µg/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.