

*Phillip Ford*

*supervising  
scientist  
report*



## **MOUNT LYELL REMEDICATION**

**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

**MOUNT LYELL  
REMIEDIATION**



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

**Peter Teasdale, Simon Apte,  
Graeme Batley & Phillip Ford**



Department of Environment  
and Land Management



*supervising scientist*

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.

Peter Teasdale, Simon Apte, Graeme Batley—CSIRO, Centre for Advanced Analytical Chemistry, Division of Coal and Energy Technology

Phillip Ford—CSIRO, Centre for Environmental Mechanics

---

© Commonwealth of Australia 1996

Supervising Scientist  
Tourism House, Blackall Street, Barton ACT 2600 Australia

ISSN 1325-1554

ISBN 0 642 24310 7

This work is copyright. Apart from any use as permitted under the Copyright Act 1968, no part may be reproduced by any process without prior written permission from the Supervising Scientist. Requests and inquiries concerning reproduction and rights should be addressed to the Research Project Officer, *eriss*, Locked Bag 2 Jabiru NT 0886.

Views expressed by authors do not necessarily reflect the views and policies of the Supervising Scientist, the Commonwealth Government, or any collaborating organisation.

Printed in Darwin by Image Offset.

## 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  $\mu\text{g/L}$ ). Elsewhere, surface water copper concentrations ranged from about 100  $\mu\text{g/L}$  in the north to 12  $\mu\text{g/L}$  in the south. Bottom water concentrations ranged from about 30  $\mu\text{g/L}$  on the delta to 4  $\mu\text{g/L}$  in the south. About 65–85% of the copper at all sites was in the filterable fraction ( $<0.45 \mu\text{m}$ ) 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 copper-laden tailings material in the northern harbour and the precipitation of colloiddally-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  $\mu\text{g/L}$  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  $\mu\text{g/L}$ . 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  $\mu\text{g/L}$  at the surface sediments and decreased to less than 2  $\mu\text{g/L}$  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 Macquarie 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.

# Contents

Executive summary	iii
Acknowledgments	ix
1 Introduction	1
2 Behaviour of copper in estuarine systems	1
2.1 Introduction	1
2.2 Fate of copper during estuarine mixing	2
<i>Mixing process</i>	2
<i>Adsorption/desorption behaviour</i>	4
<i>Effect of pH</i>	4
<i>Solution speciation and complexation by natural organic matter</i>	5
<i>Particulate copper</i>	7
2.3 Copper in Macquarie Harbour waters	8
2.4 Copper in estuarine sediments	11
<i>Geochemical speciation</i>	11
<i>Copper bioavailability in sediments</i>	13
2.5 Copper in Macquarie Harbour sediments	15
2.6 Pore waters and sediment processes	17
<i>Pore water sampling and analysis</i>	17
<i>Application of pore water peepers to sediment process studies</i>	21
<i>Copper flux measurements using benthic chambers</i>	23
<i>Plastic strip collectors in sediment process studies</i>	24
3 Methods	25
3.1 General analytical procedures	25
3.2 Field program	25
3.3 Sample preparation and analysis	28
<i>Overlying water samples</i>	28
<i>Pore water samples</i>	30
<i>Stacker samples</i>	30
<i>Sediment cores</i>	30
<i>Sediment traps</i>	31
<i>Benthic chambers</i>	31
4 Results and discussion	31
4.1 Macquarie Harbour waters	31
<i>Water column profiles</i>	31
<i>Dissolved and particulate metal concentrations in the water column</i>	32
4.2 Macquarie Harbour sediment	38
<i>Physical characterisation of the sediment</i>	38

<i>Metal concentrations in the sediment</i>	42
<i>Acid-volatile sulfide and simultaneously extracted metal measurements of the sediment</i>	43
4.3 Macquarie Harbour sediment pore waters	45
4.4 Collection of sediment species mobilised by oxidation	48
4.5 Determination of benthic and sedimentation copper fluxes in Macquarie Harbour	50
<i>Benthic copper fluxes from peeper pore water profiles</i>	50
<i>Benthic copper fluxes from benthic chamber deployments</i>	50
<i>Sedimentation fluxes from sediment trap deployments</i>	51
<i>Mass balance of copper in Macquarie Harbour</i>	52
5 Preliminary model of copper cycling in Macquarie Harbour	53
5.1 The King River delta	53
5.2 Northern Macquarie Harbour	54
5.3 Southern Macquarie Harbour	55
6 Recommendations for future work	57
6.1 Delta remediation options	57
<i>No action</i>	57
<i>Partial delts revegetation</i>	58
<i>Dredging options</i>	58
<i>Capping the delta</i>	58
<i>King River diversion</i>	58
6.2 Tailings remediation options	58
<i>Relocation of tailings within harbour</i>	58
<i>in situ tailings treatment</i>	58
7 Remediation options for Mount Lyell tailing deposits in Macquarie Harbour	58
8 Summary	59
Appendixes	61
Appendix 1 Profiles of temperature, pH, salinity, dissolved oxygen, redox potential and turbidity in Macquarie Harbour waters at sites 1 to 10	62
Appendix 2 Particulate iron, manganese and copper in sediment cores from sites 1 to 10.	72
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	82
Appendix 4 Profiles of amounts of iron and copper, and the copper/iron ratio, collected on the stackers at sites 1 to 10	100
References	111

## Figures

Figure 2.1	Idealised dilution behaviour of dissolved chemical constituents in an estuary	2
Figure 2.2	Effect of salinity on copper complexing capacity in the Severn Estuary, UK (Apte et al 1990)	6
Figure 2.3	Map of Macquarie Harbour with sampling sites and showing the general locations of the King River delta, the northern and southern Macquarie Harbour zones	9
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)	14
Figure 2.5	Multi chambered acrylic peeper 30 X 8 X 2 cm (a) plan view, (b) side view. (Drawing not to scale)	18
Figure 2.6	Pore water profiles of iron and manganese in sediments from the Georges River, Sydney NSW	22
Figure 2.7	Effect of deployment time on the deposition and mass of iron oxyhydroxide collected on Lexan strips immersed in an estuarine sediment	24
Figure 3.1	Design of the polycarbonate strip collectors used in this study	27
Figure 3.2	Photo of the benthic chamber in use at Macquarie Harbour	29
Figure 4.1	The variation of dissolved copper iron, and manganese with salinity at sites 1 to 10	35
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	36
Figure 4.3	Correlation of dissolved copper with dissolved iron and dissolved manganese at sites 1 to 10	37
Figure 4.4	Particle size fractionation with depth at sites 1 to 10	40
Figure 4.5	Areas of sediment types in Macquarie Harbour (after Department of the Environment 1975, map 4)	41
Figure 5.1	Preliminary model of copper cycling in the King River delta	53
Figure 5.2	Preliminary model of copper cycling in the northern Macquarie Harbour	55
Figure 5.3	Preliminary model of copper cycling in the southern Macquarie Harbour	56

## Tables

Table 2.1	Copper complexation capacities in estuarine waters	6
Table 2.2	Dissolved copper behaviour in estuaries	7
Table 2.3	Dissolved copper concentrations in coastal and oceanic seawater	7
Table 2.4	Metals and organic matter concentrations and complexation capacity of Macquarie Harbour waters	8

Table 2.5	Copper ( $\mu\text{g/g}$ ) in surface sediments from Macquarie Harbour	15
Table 2.6	Summary of sediment quality criteria for metals ( $\text{mg/kg}$ )	16
Table 3.1	Peeper and stacker deployment sites	26
Table 3.2	Sediment trap deployment sites	27
Table 3.3	Benthic chamber deployment sites	28
Table 4.1	Dissolved metals, DOC ( $<0.45 \mu\text{m}$ ) and salinity in Macquarie Harbour waters	32
Table 4.2	Dissolved metal concentrations ( $\text{mg/L}$ ) obtained from other studies	33
Table 4.3	Particulate metals ( $>0.45 \mu\text{m}$ ) in Macquarie Harbour waters	33
Table 4.4	Complexation capacities of Macquarie Harbour waters	38
Table 4.5	Descriptions of Macquarie Harbour sediment core samples	39
Table 4.6	Acid-volatile sulfide (AVS) and simultaneously extracted metal (SEM) concentrations in sediment cores	44
Table 4.7	Comparison of total particulate copper and acid leachable copper from sediment cores at sites 1 to 10	45
Table 4.8	Peepers found at the different site types	46
Table 4.9	Summary of copper concentrations ( $\text{mg/l}$ ) in pore water and overlying water from peeper samples	47
Table 4.10	Calculation of copper fluxes across the sediment-water interface	51
Table 4.11	Mass flux of sediment from sediment trap measurements	52
Table 4.12	Flux of copper in particulate material settling to the sediments	52

## **Acknowledgments**

We are grateful for the assistance of many people in the planning and execution of this project. Lois Koehnken provided assistance with the provision of reports and data and helped pave the way for two smooth field trips. The success of these visits was assured by the Tasmanian Department of Environment and Land Management (DELM) staff at Queenstown, Mark Stalker and his group of divers, and Ron Morrison and the crew of the Wilson's Pride. At Lucas Heights, expert analytical support was provided by Jacqui Lassau, Bobby Lovatt, Chris Brockbank, Lidija Vojnovska and John Buchanan. Lorraine Lloyd provided much needed help with the typing and figures.