

MOUNT LYELL

REMEDIATION

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Modelling of the

hydrodynamics and

chemistry of

Macquarie Harbour,

western Tasmania

GD Tong & B Williamson



supervising scientist

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.

This report should be cited as follows:

Tong GD & Williamson B 1998. *Modelling of the hydrodynamics and chemistry of Macquarie Harbour, westem Tasmania*. Mount Lyell Remediation Research and Demonstration Program. Supervising Scientist Report 136, Supervising Scientist, Canberra.

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Supervising Scientist Environment Australia GPO Box 787, Canberra ACT 2601 Australia

ISSN 1325-1554

ISBN 0 642 24339 5

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Printed in Tasmania

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Acknowledgements

Computational Fluid Mechanics Int acknowledges with pleasure the following personnel and the assistance received from them in the execution of the study:

- Hydro-Electric Commission (Mike Wallis, Barry Wise, Mark Johnston and George Jakins) for data on river flows, harbour water levels and harbour bathymetry.
- National Tidal Facility, Flinders University (Paul Davill and Seana O'Brien) for Pilot Bay harmonic constants and Granville Harbour tides.
- Bureau of Meteorology (Mal Riley) for wind data from Cape Sorell and Strahan Airport.
- Project management (Lois Koehnken, David Klessa and Warren Jones) for helpful comments on progress reporting and understanding in delays with this final report.

CFM records here its appreciation in having had the opportunity to address the modelling of the hydrodynamics and chemistry of Macquarie Harbour—a large natural harbour under encroachment from mankind in a World Heritage Area.

The Human Future depends on our ability to combine the knowledge of science with the wisdom of wildness.

Charles A Lindbergh

Executive Summary

This report documents the work carried out under Task 14 (Modelling of the hydrodynamics and chemistry of Macquarie Harbour, Western Tasmania) as part of the joint Federal/Tasmanian 'Mount Lyell Remediation Research and Demonstration Program' (MLRRDP). The report describes all aspects of the work-strategy carried out to achieve the study objective of developing a hydrodynamic and chemical model capable of estimating the effect on water quality in Macquarie Harbour as a result of changes in pollutant levels, particularly copper, entering the harbour from the King River.

Macquarie Harbour is a large roughly rectangular harbour ($30 \text{ km} \times 8 \text{ km} \times \text{up}$ to 50 m deep) on Tasmania's rugged World Heritage West Coast. It is connected to the Southern Ocean through a relatively narrow and shallow entrance channel. Being in the midst of the 'roaring forties' and with two major west coast rivers (King River and Gordon River) discharging to it, the harbour exhibits complex three-dimensional hydrodynamics under tidal, wind and freshwater forcing.

Additional to this natural system has been the discharge of copper mine tailings into the Queen River and down the King River to Macquarie Harbour at the rate of 1 million tonnes per year (copper load 2000 kg/day) for the last century.

Herein lies the backdrop to this study which sets the study objective of a working computational model. The objective has been achieved and the major tasks constituting the modelling approach are briefly reviewed here.

- Review of the available physical and chemical data.
- Configuration, verification and use of a hydrodynamic model, C3, capable of simulating the 3D hydrodynamics of Macquarie Harbour.
- Conceptualisation of the chemical speciation model and its implementation through the equilibrium model MINTEQA2.
- Embedding of the chemical model within the hydrodynamic modelling.
- Use of the integrated physical/chemical model to further understand harbour processes making full use of the available DELM data set.
- Use of the model in predicting the effects of treated loadings.

1 Review of data

The study commenced with a review of all available data to gain an understanding of the harbour in terms of its geometry, hydrodynamics and chemistry. Tidal, wind and freshwater forcing were also reviewed and much of the available data were plotted and presented in a compendium for easy access.

The chemistry data collected over DELM's 4¹/₂ month intensive monitoring period (early December 1994 to mid April 1995) was particularly valuable as a set of test data and this period was chosen as the study's test period.

2 Hydrodynamic modelling

The proposed model C3 from Seaconsult Marine Research Ltd, Vancouver, was configured to Macquarie Harbour with a 400 m \times 400 m horizontal grid resolution and a vertical resolution (from water surface) of 6×2 m + 1×3 m + 7×5 m for the deepest part of the harbour.

Taking advantage of the mode-split nature of the model and using a time-step of 2 minutes (adopted throughout the study) preliminary runs were undertaken to establish configuration of the model to the harbour. The hydrodynamic configuration process addressed freshwater plume propagation, harbour water level response, entrance channel behaviour and development of the typical steep gradient of the observed halocline structure. A detailed account of this configuration process was given in the required Interim Report MH-1-9/95.

Once configured, the model was used to assist in understanding the complexities of the hydrodynamics of the harbour. Pre-empting the modelling of the chemistry, the concentration of copper was first used as a scalar tracer (no chemical reactions taking place) to investigate the hydrodynamic response of the model (in terms of likely copper plume migration) for two prevailing wind conditions under a common tidal forcing. All hydrodynamic tests are fully described in section 3.

3 Chemical modelling

Following a review of the chemistry of Macquarie Harbour, the US EPA model MINTEQA2 was used to simulate the two processes considered to be the most important in the copper speciation process within the harbour—adsorption onto hydrous metal oxides and complexation with dissolved organic matter (DOC). Details of the application of MINTEQA2 are given in section 4.

The adsorption process was shown to be dominant and the settling out of the river-borne colloidal iron oxides was modelled by the introduction of a settling velocity to the particulate iron oxides formed by the flocculation of the colloids as they move into the higher ionic strength of the mixing zone. For the King River sediments discharging to Macquarie Harbour, this was taken from the literature to be 10^{-4} m/s for fine flocculating sediments.

4 The hydrodynamic and chemical model interface

MINTEQA2 is an equilibrium model and the proposed modelling strategy was to embed MINTEQA2 within the hydrodynamic model for use, in a pseudo-transient manner, by continually updating it with a changing chemical field. The validity of this strategy depends on the equilibrium speeds of the MINTEQA2 chemistry and the hydrodynamic transport of the four quantities involved in the adsorption and complexation processes (concentrations of Cu, Fe, DOC and salinity for pH).

The approach to embedding MINTEQA2 within C3 was via the pre-computation of a set of 'look-up' tables to be interrogated for % adsorbed and % complexed total Cu and defined over the expected range of the 4-parameter space for Macquarie Harbour. Interrogation of the tables was efficiently achieved by two bi-linear interpolations, one in the Cu-pH plane and the other in the Fe-DOC plane. Toxic copper (free copper ions) was also uniquely available from the MINTEQA2 speciation.

5 Model proving tests

The model was run over the $4\frac{1}{2}$ month intensive monitoring period with the appropriate hydrodynamic forcing and the measured King River chemical loadings. Results were compared with the measured harbour data and presented in a range of graphical formats (section 5).

Two sets of plots are of particular importance since they compare model results with measured results.

The time-series plots over the full period at 6 DELM monitoring stations in the northern harbour for top, mid and bottom of the water column (figs 5.1 to 5.6).¹ These plots show good agreement with the weekly copper measurements and indicate both the dominance of the adsorption/fall-out mechanism and its validity in the northern harbour.

The profile plots at 11 DELM monitoring stations in the southern harbour (figs 5.28 to 5.38) which show the conservative copper model as applicable on and south of the Sophia Pt–Liberty Pt transect.

6 Model predictions

The model has been used to predict the effect of selected reduced copper loadings and commensurate reduction in loadings of the hydrous metal oxide adsorbing surfaces (Fe, Al and Mn) provided as two-point data by project management.

For the representative electrowinning solvent extraction process with a pH of 5.5, these tests were for reduced loadings designated Stock 2 (80% treated) and Stock 3 (99% treated). Timeseries of loadings were derived by assuming flow dependency and linearly interpolating between the two given data points corresponding to Burbury Power Station being either off or on. (For Stock 2, these were scenarios 8 and 11 respectively whilst for Stock 3, they were scenarios 9 and 12 respectively as designated by project management.)

Results have been consistently compared with the untreated case running over the adopted 4½ month test period of DELM's monitoring of the King River loadings and weekly profiling measurements of the harbour's responses. The comparisons show the expected marked decrease in water column copper concentrations as a time-series over the test period.

In the longer term and perhaps more interestingly, since adsorption with fall-out of colloidal sediments is dominant, is the comparative cumulative deposition plot at the end of the report which shows the decrease of copper to sediments for the treated cases to be consistent with the percentage reductions in loadings. This result reinforces the finding that most of the copper deposits out with the settling of the sediments that form the King River delta.

7 Concluding remarks

The modelling procedure has proved better than expectations held at the commencement of the study. This positive assessment is largely based on the time-series plots (figs 5.1 to 5.6) and the profile plots (figs 5.28 to 5.38) that constitute a comprehensive comparison of chemical processes modelled, untreated/treated scenarios and the DELM field measurements taken in Macquarie Harbour over the $4\frac{1}{2}$ month test period.

No doubt the study could benefit from refinements such as further calibration of the hydrodynamics from moored current meter data and refined grid modelling of the northern harbour, particularly around the King River delta, to better resolve the deposition process. An

¹ With the exception of figures 4.0 to 4.5, all figures are located in the appendix.

addition to the model expected to yield improved results would be the inclusion of the uptake of copper from the sediments throughout the harbour.

Nonetheless the study has yielded some interesting results as follows.

- King River plumes disperse quickly with the majority of the copper adsorbing to hydrous metal oxides which undergo colloidal sedimentation and fall-out close to the mouth forming the delta region. (Residual water column copper being well-modelled by the adsorption, deposition and complexation process.)
- Toxic conditions (indicatively 3×10-9 M) were reached throughout the southern harbour over the 4½ month test period and were well-modelled by the conservative case.
- Typical proposed treatment scenarios for acid mine drainage will achieve the expected beneficial results (commensurate with the level of treatment) on the water quality in Macquarie Harbour with much less copper depositing and transporting within the water column.
- The proposed treatment scenarios will achieve reduced concentration levels in the region around Yellow Bluff which are generally below the indicative level for potentially 'toxic' conditions (3×10-9 M) for typical tidal conditions and moderate to strong south-westerlies and north-easterlies. This result is of interest in regard to the region as a potential fish-farming site.

Colour copies of the figures can be obtained from Gail Barrowcliff at the Environmental Research Institute of the Supervising Scientist Locked Bag 2, NT 0886.

A charge may be associated with their supply.

1 Introduction

Macquarie Harbour is a large coastal water body covering some 250 km² of Tasmania's rugged west coast. With a mid-harbour latitude of about 42° 20' S, the harbour is centred in the ocean tract, the 'roaring forties', amidst part of a World Heritage area. Its narrow and relatively shallow entrance channel connecting to the Southern Ocean makes it one of the largest natural harbours in the southern hemisphere.

Two rivers enter the harbour, the King River in the north-east corner and the Gordon River at the southern end. From the King River, Macquarie Harbour has been receiving copper mine tailings at the rate of about 1 million tonnes per year for 100 years with a copper load estimated to be about 2000 kg/day.

The extreme adverse effects on the environment from this level of pollution has been recognised as a major environmental disaster prompting the Tasmanian and Commonwealth Governments to combine in the implementation of the Mount Lyell Remediation Research and Demonstration Program (MLRRDP). This program comprised some 16 research tasks of which the 'Modelling of the Hydrodynamics and Chemistry of Macquarie Harbour' was designated study 14.

Computational Fluid Mechanics Int (CFM) Pty Ltd tendered for this task in late April 1995 and commenced work about a month later. This document reports the work and results of the study. It follows two previous submissions, a compendium of the available physical and chemical data (July 1995), compilation of which initiated the study and the required Interim Report MH-1-9/95.

2 Study overview and main strategies

2.1 Site location and bathymetric description

The location of Macquarie Harbour (in terms of AMG eastings and northings) and its bathymetry (with reference to AHD) is given in figure 2.1. As detailed in the Interim Report, the bathymetry was extracted from four sources.

- 1. Soundings for the northern part of the harbour taken by the HEC and contoured to AHD 83 in the 1:25000 HEC plan No. G310587.
- 2. Entrance bathymetry taken from Admiralty Chart AUS 177 compiled from 1991 hydrographic soundings. (In using this data, mean lower low water at Cape Sorell was taken to be approximately AHD since AHD generally coincides with a low water mark.)
- 3. Depth to bottom data taken from the several water quality profiling exercises undertaken on the harbour since May 1993. (The profiling depth (+1 m) was taken as indicative of the bathymetric depth to AHD since the tidal range in Macquarie Harbour is not large, within about 0.5 m which is within the error bars of the rest of the bathymetric data.)
- 4. Limited HEC sounding data taken in March 1993 along radial transects out from the west bank just north of the Gordon River mouth.

2.2 Study objective

The principal objective of this study was to produce a proven integrated hydrodynamic and chemical model to be used for the prediction of copper concentrations within Macquarie Harbour from copper loadings (measured and proposed) entering the harbour via the King River.

(Following the results of test runs providing insight into the time scales of dominant physical and chemical mechanisms, the 4½ month period of weekly copper monitoring carried out by the Tasmanian Department of Environment and Land Management (DELM) was chosen. This period, from early December 1994 to mid April 1995, was recognised as a meaningful term over which computations should be run in regard to chemical processes modelled and hydrodynamic conditions represented.)

2.3 Data base assembly

In a computational study of this nature, comprehensive use of the available data base is necessary at two stages, first in establishing what might be possible as a plausible modelling procedure and second, in the verification of a resulting model's performance.

Available physical and chemical data, collected as part of the DELM Macquarie Harbour– King River Study (Koehnken 1996), were reviewed early in this study and presented as a compendium in the following format:

- Plotted profiles of temperature, salinity, pH, DO and Redox for the 'monthly' data at 20 profiling stations grouped as a summer and winter series of profiles (September 1993 to May 1995).
- Tables of 'monthly' copper data (suspended sediment, ASV Cu and Total Cu) at top, mid and bottom locations in the water column for all profiling stations and at about bi monthly intervals from May 1993 to May 1995.
- Plotted profiles of pH, salinity, DO and turbidity for the 'weekly' data at 6 stations in the northern harbour grouped as a 6-month series of plots from December 1994 to May 1995).
- Tables of 'weekly' copper data (Total Cu) at top, mid and bottom locations in the water column for 10 stations in the northern harbour from 5th December 1994 to 31st May 1995.
- Time-series of hourly King and Gordon River discharge (May 93 to March 95).
- Time-series of water levels at Beacon 8 (September 93 to April 95).
- Stick vector plots of daily mean winds at Granville Harbour (May 93 to March 95).

Example profiles of monthly data at four DELM profiling stations (11, 12, 13 & 14) across the representative Sophia Pt–Liberty Pt transect for the summer and winter series are given in figures 2.2 and 2.3 respectively. These stations are located at approximately equal intervals running north to south in order along the transect. (See fig 5e for the mean location of measuring stations from December 93 onwards.)

(This main volume was supplemented with a second volume (Vol 2) giving the tables of monthly profile data for all stations over the harbour.)

2.4 Approach to the modelling

The approach to the modelling has been to establish a 3D hydrodynamic model of Macquarie Harbour under marine (tidal and salinity), wind and freshwater forcing to provide a velocity vector field for the transport of salinity and the other scalar chemical constituents entering the harbour from the King River. Once within the harbour, chemical constituents were subject to chemical processes considered to be dominant in the speciation of copper.

These key chemical processes, elucidated below and discussed in detail in section 4, were considered to be the adsorption of Cu onto hydrous metal oxides (Fe, Al and Mn) and the complexation of Cu with dissolved organic carbon entering the harbour from both the King and

the Gordon Rivers. The scalar variables required to be transported within the harbour were hence taken to be: total Cu, a mole equivalent hydrous ferric oxide (representing the hydrous metal oxides as adsorbing surfaces), dissolved organic carbon and salinity from which pH was determined.

For the 3D hydrodynamic modelling, the use of the Canadian model, C3, from Seaconsult Marine Research Ltd, Vancouver was proposed. For the chemical speciation model the USEPA equilibrium model, MINTEQA2, was proposed as being an 'off the shelf' chemical equilibrium model considered to have the capability of modelling copper speciation (adsorption and complexation) pseudo-dynamically through a series of equilibrium states. Chemical equilibrium was assumed to be rapidly attainable in an ever-changing field of chemical constituents undergoing continuous transport and reaction within the harbour.

2.5 The 3D hydrodynamic model C3

2.5.1 Description

Nomination of the C3 hydrodynamic model was in accordance with CFM's policy of using the best available hydrodynamic models in engineering practice. The C3 model is the latest variant of the Canadian GF8 model (Crean et al 1988 a & b) which is a derivative of the well-known North Sea model developed by JO Backhaus in the 1980s (Backhaus 1985). This model has been extensively tested on the highly baroclinic and complex flows in the waters between Vancouver Island and the Canadian mainland as reported in Stronach et al 1993.

Following long-standing collaborative links with SMR, the choice of C3 enabled CFM to approach the modelling task with a base hydrodynamic model in which it had confidence and moreover, full control of source code, essential in the interfacing of a chemical model.

The model is described in detail in the paper by Stronach et al 1993. It is based on the usual equations for a three-dimensional description of nearly-horizontal flow:

- two conservation of momentum equations, one for each of the two horizontal coordinate directions but including vertical advection and diffusion;
- a mass conservation equation which is used to yield vertical velocity under the nearlyhorizontal flow assumption;
- a salt conservation equation;
- the hydrostatic equation;
- an equation of state linking salinity and density.

The model is discretised on the well-known Arakawa C finite-difference grid.

Two features of the model which are major factors in its performance are as follows.

- 1. It is a semi-implicit model achieved by a mode-splitting technique in which the barotropic mode associated with the free-surface wave is treated implicitly as a separate free-surface computation. This leaves the baroclinic motion to be solved explicitly without the very restrictive time-step that the Courant condition would otherwise place on such explicit computations had the barotropic free-surface computations not been decoupled. The procedure allowed a time step of 2 minutes to be used with a grid cell size of 400 m \times 400 m.
- 2. The advective transport part of the model is equipped with a flux correction procedure for the accurate transport of scalars as described in Zalesak 1979. This was always seen as an important feature of the model in view of the need to accurately transport scalar fields

throughout the harbour for chemical speciation (concentrations of salinity for pH, copper, hydrous ferric oxide and dissolved organic carbon).

2.5.2 Application of C3 to Macquarie Harbour

Model C3 was configured to Macquarie Harbour using a 400 m \times 400 m rectangular grid as shown in figure 2.4. The data requirements of the model are as expected for hydrodynamic computations with the following data and boundary conditions being used.

- Bathymetric data as given in figure 2.1.
- Tidal forcing using the model's prediction routine and the harmonic constants of the 4 main constituents for Pilot Bay as obtained from the National Tidal Facility (amplitude in metres, phase in degrees): M2(.11, 319), S2(.10, 57), K1(.19, 58) and O1(.14, 28).
- Freshwater discharges for the King River (hourly) and the Gordon River (daily).
- Wind velocities at Cape Sorell (hourly) and factored down by a $\frac{1}{3}$ rd for use in the model to be more consistent with the wind record from Strahan Airport (nominally half-hourly but irregular in time and more difficult to use).

Preliminary work was undertaken on the development of realistic baroclinic harbour conditions in the period leading up to the Interim Report and is comprehensively reported therein. A vertical grid resolution of 6×2 m + 1×3 m + 7×5 m layers (at the deepest part of the harbour) was adopted which was found to allow appropriate freshwater propagation into the harbour and salt fluxes through the harbour entrance, Kelly Channel.

'Cold start' (static) initial conditions were used, first with a uniform salinity and then with a salinity ranging from 23 ppt at the surface to 31 ppt in the deepest part of the harbour with the model spinning-up to its typical sharp stratification over a few weeks.

At the completion of the Interim Report, the model had been configured, through a series of trial tests (varying channel geometry and vertical diffusion) to accurately reproduce the salinity structure within Macquarie Harbour by comparison with DELM profiling field measurements. With a view to using salinity as an indicator variable for pH, this was taken as an appropriate point to begin introduction of the chemical model.

2.6 The chemical speciation model MINTEQA2

2.6.1 Description

MINTEQA2 is a chemical thermodynamic equilibrium model developed by the US EPA for computing the speciation of chemical entities (as represented by the equilibria between dissolved, adsorbed, solid and gas phases) in dilute aqueous systems (environmental water bodies). The present model (Allison et al 1990) has evolved through a series of earlier versions (Brown & Allison 1987) and (Felmy et al 1984).

2.6.2 The interface between the hydrodynamic and the chemical model

The interface between the hydrodynamic and chemical models was chosen to be implemented as an interpolation procedure of a 4-parameter space for the chemistry of Cu speciation, predetermined from MINTEQA2 and presented as % adsorbed and % complexed total copper. This enabled all MINTEQA2 chemistry to be pre-computed over a full range of possible parameter values (concentrations of total Cu, Fe, DOC and salinity for pH).

The interpolation procedure was established as two bi-linear interpolations, one in the Cu-pH plane and the other in the Fe-DOC plane. The interpolation routine was entered as a computational 'look-up' table each time step with the hydrodynamically computed values of

the four parameters and exited with the % adsorbed and % complexed total copper. (The concentration of free copper ions (the toxic component) was also obtained from the 'look-up' tables as a further unique 5^{th} parameter concentration in the MINTEQA2 speciation.)

An important part of the interfacing of the chemical model with the hydrodynamic model was the imposition of a modified vertical velocity field to include a settling velocity chosen to be representative of the fine colloidal particles that have deposited out forming the King River delta. This settling velocity (van Leussen 1988) was applied to the hydrous ferric oxide constituent and a continually updated proportion of the total Cu as determined from the % adsorbed.

2.6.3 Application of MINTEQA2 to Macquarie Harbour

The input requirements for the chemical model are the copper loadings and the concentrations of the quantities involved in the chemical processes as they are transported down the King River and enter Macquarie Harbour.

Concentrations of the hydrous oxides of Fe, Al, Mn provide adsorbing surfaces for the copper. The hydrous oxides of Al and Mn were found as mole equivalents of hydrous ferric oxide so that the concentration of just the one characteristic adsorbing surface (equivalent hydrous ferric oxide) was required to be transported within the harbour. The concentration of dissolved organic carbon from both rivers was also required allowing complexation of copper to occur as a competing speciation mechanism.

Once within Macquarie Harbour, in addition to the boundary inputs, salinity was also traced as a surrogate variable for defining pH via an empirically determined salinity-pH relationship taken to be unique. This assumption is clearly questionable since King River water and Gordon River water (brought in as freshwater discharges of 0 ppt) both contribute to resulting salinity and can be different in terms of their acidity. The assumption relies on the strong buffering effect of seawater on pH for credibility.

The graphical representation of the results from MINTEQA2 applied to the full range of conditions expected within Macquarie Harbour for concentrations of total copper, metal hydrous oxides, dissolved organic carbon and pH can be previewed in figures 4.6a to 4.6d.

2.7 The test period

The test period was chosen to be the time of DELM's weekly copper sampling in Macquarie Harbour, a 4½ month period from the beginning of December 1994 through to mid April 1995. This was the obvious period over which to run the computations given the available field measurements to be utilised and the loadings measured in the King River as model inputs.

The hydrodynamic forcing for the period can be previewed in figures 5abcd and the loadings for the chemistry in figure 4.1. The copper loading over the period is given in detail in figure 5.0 for the untreated (as measured) case and the two proposed treated scenarios represented by the electrowinning solvent extraction process with a pH of 5.5.

The limits of the loading components (Cu and metal oxides, Fe, Al and Mn) for the two treatment scenarios, Stock 2 (80% treated) and Stock 3 (99% treated), as provided by project management, were set by the Burbury Power Station taken to be either 'on' (86,856 l/s) or 'off' (6,856 l/s). Linear flow dependent apportioning for Cu, Mn and Al concentrations between these two limits was used. This enabled a time-series of loadings (boundary inputs) to be constructed such that comparative runs for the different treatment scenarios could be made. Constructing loadings for the treated cases in this way occasionally results in higher loadings than for the untreated case down at very low loads (see figure 5.0).

Table 1 provides a summary of the model results extracted at various intervals over the test period to illustrate designated aspects of the modelling investigation.

Figures	Purpose	Time period
3.0–3.32	Hydrodynamics of Macquarie Harbour	00:00 27-Jan-1995 to 00:00 28-Jan-1995 (hourly)
3.34	Copper deposition	17:00 30-Jan-1995 to 20:00 31-Jan-1995 (2 and 6 hourly)
3.41–3.46a	Migration of copper plume events	03:00 04-Mar-1995 to 07:00 05-Mar-1995
		03:00 19-Mar-1995 to 07:00 19-Mar-1995
4.7a–4.7d	Copper retention in water column	06:00 27-Jan-1995 to 18:00 3-Feb-1995 (twice daily)
5.1–5.6	Comparison of field measurements, treatment and process scenarios at top, middle and bottom depths	00:00 1-Dec-1994 to 24:00 13-Apr 1995 (time-series)
5.7–5.16	Comparison of treatment scenarios all with adsorption and complexation - Total Cu	00:00 31-Dec-1994 to 00:00 31-Mar-1995 (every 10 days)
5.17–5.26	Comparison of treatment scenarios all with adsorption and complexation - Toxic Cu	00:00 31-Dec-1994 to 00:00 31-Mar-1995 (every 10 days)
5.27a–5.27b	Total Cu concentrations - untreated conservative run	00:00 10-Jan-1995 to 00:00 11-Mar-1995 (every 20 days)
5.28–5.38	Comparison of field measurements and computed profiles at 11 field stations - Salinity and Total Cu	selected times between 18-Jan-1995 and 23-Mar-1995
5.39	Comparison of treatment scenarios - cumulative copper deposition	from 1-Dec-1995 until 10-Apr-1995

Table 1 Result sequences over the test period 1-Dec-1994 to 13-Apr-1995

3 The Hydrodynamics of Macquarie Harbour

3.1 Overview

The location of Macquarie Harbour, its bathymetric shape and main physical features have been presented in section 2 above. Here the hydrodynamics of the harbour is addressed in order to obtain some understanding of the three-dimensional current patterns which may be occurring within the harbour and which are central to the transport of all the scalar quantities governing the chemistry of the harbour. Overall Macquarie Harbour can be described as a broad estuary with very substantial freshwater discharges and a highly constrictive entrance to the Southern Ocean. The freshwater discharges are essential to the strong stratification which persists, year around, with a well defined halocline in the top 10 to 14 m. So too are the entrance characteristics which cause marine (tidal) effects to be heavily damped through the harbour entrance thus limiting tidal effects (wave propagation and mixing) while still allowing the essential salt feed. The situation gives rise to a complex estuarine response.

The key hydrodynamic response for Macquarie Harbour can be summarised as follows. Although the entrance is restrictive in terms of wave propagation, it is sufficient to allow a salt flux into the body of the harbour which, over time and along with the freshwater discharge, maintains a strong stratification with a longitudinal salt gradient through the upper layers of the harbour.

(The halocline generally resides in the top 10 to 14 m of the surface waters and exhibits a fairly linear gradient of typically 14 ppt in 4 m. This translates to a system with a high degree of

static stability as given by a Brunt-Väisälä frequency, N, of 0.16 s⁻¹ $\left(N^2 = -\frac{g}{r}\frac{fr}{fk}\right)$. For comparison, values of N in the large gradient regions of the thermocline in the upper layers of the open ocean are typically 0.01 s⁻¹ (Gill 1982, p52).)

As might be expected, this hydrodynamic scenario results in the harbour exhibiting tidally influenced behaviour in just that portion near the entrance (the northernmost 25% to 30%) while over its main body, the behaviour is more like that of *closed basin circulation* under baroclinic forcing (density effects) and wind forcing (both direct through surface wind stress and indirect through wind set-up of water levels). Being a wide harbour, about 8 km across on average, the Coriolis effect will also be present to compound the baroclinic response. Such characteristic behaviour is now examined in some detail below.

3.2 Hydrodynamic forcing

Typical forcing function data such as tidal levels, wind, river discharges and harbour salinities have been introduced in CFM's Compendium of Data and Interim Report MH-1-9/95. For the test period (as nominated above) they can be previewed here in figures 5abcd.

3.3 Basic hydrodynamic mechanisms

A broad conceptual picture of currents in Macquarie Harbour has been drawn in the DELM Macquarie Harbour–King River Study (Koehnken 1996).

Whilst these general ideas on the complex current behaviour may well be applicable under some circumstances, it is important to consider the widely varying response of the harbour to a range of forcing scenarios which can be rapidly changing.

The broad conceptual ideas arising from the DELM study demonstrated the need for a 3D hydrodynamic model and results from the 3D modelling of this study are now used to help develop a detailed understanding of Macquarie Harbour hydrodynamics.

Results of running the model over the $4\frac{1}{2}$ month test period are examined at various periods and time intervals (frequency of examining results) depending on what is being examined and what inferences are expected to be drawn from the results.

The first detailed examination is for an understanding of the basic hydrodynamic mechanisms over a period commencing at 0000 hrs on the 27th January 1995 and proceeding for 24 hrs at 1 hr intervals.

Figure 3.0 shows the phased tidal response within the harbour (entrance conditions and harbour at large) compared with the tidal forcing of the Southern Ocean (Pilot Bay). Four features are immediately apparent.

- 1. The heavy attenuation of the tidal response within the harbour compared to the tidal range of the Southern Ocean. (The ocean tide being predicted from the 4 major tidal constituents (M2, S2, K1 and O1) for Pilot Bay just outside the entrance to Macquarie Harbour.)
- 2. The 'perched' nature of the water level in Macquarie Harbour (mean harbour levels being higher than mean sea levels) due to freshwater inflows.
- 3. The phase lag of about 4½ hours on peaks and 6½ hours on troughs between the ocean tide and the tidal behaviour over most of the harbour.
- 4. The tidal behaviour just inside the harbour (Station 19) which shows a phase lag with the ocean tide of about half that elsewhere in the harbour. Being in the entrance channel (a

region of high kinetic energy and head loss), the peaks (influenced by freshwater inflow) do not reach those of the main body of the harbour but the troughs fall lower.

Figure 3.1 gives the currents in the surface layer (top 2 m) at the beginning of the period. Tidal inflow is observed through the harbour entrance (Kelly Channel) as expected from the water level difference between the ocean (Pilot Bay) and the harbour. More surprisingly is the current along the north-west axis from the southern part of the harbour (Sarah Island) and generally over much of the harbour's width.

An examination of the recent wind history shows a consistent 10 knot south south-westerly over several hours which has dropped off to a couple of knots at 0000 hrs on the 27th. The north-west directed current is therefore only weakly wind driven at best and is better explained in terms of a surface return current as part of a large vertical circulation extending over much of the depth of the harbour basin. This is seen to be the case from figure 3.2 which is a longitudinal section of horizontal velocities and salinity contours down the centreline of the harbour.

In the absence of appreciable along-axis winds, the vertical circulation shown in figure 3.2 derives from the longitudinal water surface gradient and salinity gradient both of which are present at the time (from historical wind set-up and tidal inflow) to drive NW to SE baroclinic undercurrents in a closed basin. These longitudinal gradients are given in figure 3.3 along the centreline (k=30) and two parallel longitudinal sections (k=27, 1200 m to the south and k=33, 1200 m to the north). Figure 3.4 is a contour plot of the water surface elevation at 0000 hrs on the 27^{th} . It clearly shows the set-up on the water surface and helps to explain some of the flow patterns depicted by the surface velocity vectors in figure 3.1.

The pattern remains at 0100 hrs (fig 3.5). At 0200 hrs (fig 3.6) the wind has started to develop as a northerly providing a direct wind stress effect to combine with a relaxation of surface setup and tidal inflow in establishing a general north to south flow in the surface layer. This response continues to develop from 0300 hrs through to 0600 hrs (figs 3.7 to 3.10) where the tidal flow has just started to reverse to an outflow. The wind has also just swung to an east south-easterly blowing up the harbour at about 4 knots but the inertia in the system has not as yet been reversed and the north to south flow in the surface layers continues. Figure 3.11 is another longitudinal section plot of horizontal velocities and salinity contours down the harbour centreline. This plot again clearly shows the vertical circulation typical of baroclinic flows in closed basins. The fact that it is now reversed to what it was just a few hours earlier is important in gaining a notion of the time scale of the hydrodynamics which governs the transport of the quantities of interest in this study.

Figure 3.12 is the accompanying contour plot of surface elevation over the harbour. Here, water surface gradients over the body of the harbour are seen to be less than at 0000 hrs albeit at a higher level because of inflows. There has been little wind to cause any pronounced water surface set-up and the longitudinal alignment of the contours indicate almost level conditions over the central body of the harbour. For the ends of the harbour, there is a surface slope from the north-east corner and at the southern end, one to the south-east. These slopes appear to be driving the north to south directed surface currents.

The harbour behaviour from 0700 hrs to 1300 hrs is depicted in figures 3.13 to 3.19. This is over the first 6 hours of the tidal outflow in which the water surface level drops over the harbour and the flow dynamics as at 0600 hrs continues. This shows the prolonged tidal outflow and what can be described as bathymetry induced 'upwelling' (the seaward return flow in the more saline lower layers being directed upwards by basin bathymetry just northward of the Sophia Pt–Liberty Pt transect). The wind remained quite low over this period and, if

anything, was directed across the harbour such that along-axis water surface set-up did not occur.

At about 1400 through to 1600 hrs (figs 3.20 to 3.22), tidal outflow continuing, a small water surface slope from the south to the north develops but still the salinity gradient is from the north to the south throughout the water column. An almost null velocity field over most of the harbour (except for the tidal outflow) gives way to a south to north flow in the upper layers with a return north to south flow below. Figure 3.23 is a further longitudinal section along the centreline of the harbour which shows the outflow through the upper layers and still the inducing of vertical circulation with north to south directed flow in the lower layers. Figure 3.24 is the corresponding contour plot of the surface elevation over the harbour and shows the contours aligned both across and along the harbour. The 0.32 m and 0.34 m contours still have predominantly a longitudinal alignment and coincide with the null horizontal velocity region shown in figure 3.22. The pattern establishes itself to 1900 hrs (figs 3.25 to 3.27) after which the tidal flow through the entrance is expected to turn. This is indeed the case and the pattern of tidal inflow and south to north directed surface flow in the southern harbour is observed over the next 5 hours to 2400 hrs (figs 3.28 to 3.32). This completes one cycle of the diurnal tide. Conditions are found to be similar to those 24 hours earlier except that the wind stress has not been conducive to establishing a water surface set-up in the top north-east corner of the harbour.

3.4 Calibration of hydrodynamic model

The calibration of the hydrodynamic model was substantially reported in the Interim Report MH-1-9/95. No reliable hydrodynamic data set (ideally a velocity time series) was available to calibrate and verify the model but the halocline structure, being fairly constant over the seasons, provided a target condition for the model to achieve and maintain. Such an exercise both tests the essential propagative and transportive capability of the model and provides an opportunity for assessing and tuning along the following lines.

- Tidal propagation.
- Surface propagation of freshwater river plumes.
- Salt fluxes through the main sea entrance (geometry influenced).
- Vertical mixing.

For the calibration of the model as reported in the Interim Report, it was found that the observed halocline structure with steep gradient through the surface layers could be achieved and maintained with the freshwater river discharges and salt fluxes entering the harbour through a realistic geometrical representation of the entrance channel. Numerical diffusion was not present to any significant extent enabling the steep gradient (typically 14 ppt in 4 m) to be maintained.

3.5 Sedimentation test

While considering the hydrodynamics of the harbour it is worthwhile previewing the sedimentation process which is a hydrodynamic process in that colloidal particles deposit out with a settling velocity. In terms of the study objectives of quantifying copper speciation, through the chemical adsorption process in MINTEQA2, the sedimentation can be expressed in terms of copper depositing on the harbour bottom. Again, any appreciation of time and space scales arising out of the test is of value.

This preview of the sedimentation aspect of the model is given for the fall-out of an isolated peak copper loading occurring at about 1600 hrs on the 30^{th} January 1995 (see fig 3.33). The resulting sedimentation is depicted in figure 3.34 for a settling velocity of 10^{-4} m/s (van Leussen 1988) which is at the low end of the range for flocculating fine sediments. Eight plots are given, the first just an hour after the peak loading showing virtually no copper deposited. The next three plots are at 2-hourly intervals to 2300 hrs showing a steep increase in copper deposited in the first 6 hours. The maximum copper deposited occurs some 10 hours after the peak in the loading (fifth plot at 0200 hrs on the 31^{st} January 1995) after which there is very little increase in maximum copper deposited as shown in the last three plots at 6-hourly intervals. Spatially, the bulk of the copper and colloidal sediments are falling out close to the river mouth in line with the known river delta formation.

3.6 Test on the ADCP data

Hydrodynamic model C3 was run over the month of September 1993 up to and including the period of the three-days of the ADCP exercise, the 29th September to 1st October 1993. Field data for this exercise was available in digital form along with the written report (Lawson & Treloar 1994).

Figure 3.35 provides the hydrodynamic forcing for just the three days of the ADCP exercise although predicted tides, river discharges and winds for the full month were used in the test.

Results of the comparison between the computed velocities and the ADCP measurements with annotated times are given in figures 3.36 to 3.38. Considerable attention, including checks with Lawson and Treloar, was given to ensuring the best possible comparison was being made in terms of spatial locations and ADCP bin depths.

Unfortunately the comparisons show very little matching. On the whole the ADCP velocities are considerably larger than the modelled velocities. Predicted tides and factored winds forcing the model should be kept in mind as possible contributing factors to this discrepancy. Further, the ADCP results exhibit considerable self-inconsistency in terms of:

- large directional variability between adjacent vectors in the same layers;
- little gradation in magnitude of velocities from the surface layer to the 9 m layer;
- a diametrically opposed response in the surface layer to the 15 knot northerly blowing for some 6 hours on the morning of the 1st October.

Overall this comparison proved of little value in the verification of the modelled hydrodynamics.

3.7 Measurements in entrance channel

The modelling of the correct salt flux through the entrance channel was found to be important in the early configuring of model C3 to Macquarie Harbour in order to achieve the observed stratification (see Interim Report).

A site visit to the harbour from the 11th to the 14th October 1995 provided an opportunity to undertake a profiling exercise in the entrance channel over 24 hrs using CFM's profiling rig based on the UCM40 MkII ultrasonic current meter. This 'on-line' instrument includes sensors for conductivity (salinity), temperature, depth, direction and tilt making it ideal for gaining an understanding of salt fluxes through the entrance.

The 24 hours of monitoring started in calm conditions at 1300 hrs on the 12th October which, after 2 hours, gave-way to very strong northerlies (north north-easterlies to north north-

westerlies up to 30 knots) over most of the monitoring period (15 hours). The last 7 hours saw a wind shift from the north-west to the south-west with speeds again up to 30 knots.

Figure 3.39 shows the tidal and wind forcing with corresponding fluxes (along-channel component of velocity and salinity) as measured in Kelly Channel just a little further into the harbour than the location of DELM station 19 given in figure 5e. The results clearly show the stratification over the first 5 hours of monitoring and the associated variation in currents through the water column during what is essentially inflow (negative along-channel velocity).

The velocity and salinity structure is very much easier to interpret in the complete profiles of figures 3.40a and 3.40b which again show the early inflow of ocean water under a top fresh layer exhibiting wind and baroclinic effects. At 6 hours into the monitoring (1900 hrs) the stratification has all but disappeared and the entrance flow has switched to outflow, uniformly fresh through the water column and which continues for the next 4 hours. At 0000 hrs on the 13th October the tide has turned to become inflow again which quickly builds in magnitude and changes in salinity (uniformly through the water column) from fresh (that water just previously moved out of the harbour) to marine in 3 hours. The uniform inflow continues to 1200 hrs (a further 8 hours) at which time slack-water is again reached and the monitoring stopped.

This entrance flow was not simulated with the model mainly because of the lack of a reliable ocean level boundary condition. Under such storm-surge effects a predicted tide will be an under-prediction of the water level forcing. Attempts to obtain a reliable water level forcing were made through discussion with the National Tidal Facility who suggested the possibility of adding the storm-surge residuals for Hobart. This addition is shown in figure 3.39 but was considered to require much further research before being adopted as a means of devising a model boundary condition. For example, research along the lines of extraction of earlier Granville Harbour residuals (observed minus predicted levels) and the correlation of these with corresponding wind records and barometric pressure to derive an appropriate offset.

3.8 Migration of river plumes

As a forerunner to model predictive runs, it is useful to gain an idea of plume migration and resulting concentrations for typical copper loadings from the King River entering the harbour and migrating within it under time-varying tidal and wind conditions. The exercise is primarily intended as an hydrodynamic issue and is investigated by tracking a conservative tracer (typical copper loading used without modification by chemistry).

From an analysis of the total available wind record for the region (Cape Sorell and Strahan Airport as obtained from the Bureau of Meteorology), predominant winds can generally be categorised as follows. (See accompanying wind roses from the Bureau of Meteorology, figs 3.41a and 3.41b.)

- From October through to March the winds exhibit both a strong southerly component (Cape Sorell) and a strong westerly component (Strahan) and predominantly occur in the sector from the south to the north-west.
- From April through to September the winds have a strong northerly component and predominantly occur in the sector from the north-west to the north-east.

On the basis of local knowledge and in broad agreement with the Bureau's statistical analysis, generally the winds over Macquarie Harbour are considered to be predominantly from the south-west or the north-east.

3.8.1 Analysis with SW and NE winds

The question of typical plume migration was first addressed by selecting for examination, two periods from the overall test period in which there is a well defined pulse of copper entering the harbour with winds from the two predominant directions over several hours. The two periods commencing 4th March (wind from the NE) and 19th March (wind from the SW) were chosen for the following reasons.

- The pulses were isolated events so that there impact could be easily tracked.
- Tidal conditions were similar for the two periods.
- King River and Gordon River flows were also similar for the two periods.

The hydrodynamic forcing is given in figure 3.42 and the copper loadings entering the harbour on the 4^{th} and the 19^{th} are given in figure 3.42a.

Results from the conservative runs (no chemistry activated and the copper acting as a conservative tracer) are given over 28 hours. (Figures 3.43 (resulting copper concentrations) and 3.43a (velocity vectors) for the 4th March and similarly figures 3.44 and 3.44a for the 19th March.)

Four immediate observations can be made.

- 1. The peak loading can be seen to enter the harbour and the associated elevated concentrations remain for some 16 to 20 hours before dropping back to harbour levels prior to the event loadings.
- 2. The effect of the wind on the hydrodynamic transporting field is not as dominant as expected and although it remains an influence the northern harbour hydrodynamics is also largely influenced by tidal forcing.
- 3. Some overall wind effect can be seen, particularly in the early stages of the plots in which there is a movement of the plume towards the harbour entrance under the NE wind (4th March) and a holding-up of the plume into the north-east corner of the harbour under the SW wind (19th March).
- 4. The plume does not appear to advect quickly away from the King River mouth but rather, within the time frame of the dispersion depicted (28 hours), to remain around the King River delta area and to diffuse into the surrounding waters. (Aerial photographs taken on the 14th October 1995 clearly showed a plume foam line typical of a river discharge turbulently diffusing into a receiving water body rather than experiencing appreciable advection under cross flow.)

3.8.2 Plume migration following injection into the free-stream

The fourth observation above suggested that it would be of interest to examine the plume migration if the plume was injected as a point source further into the harbour in more 'free-stream like' conditions.

There is some justification in carrying out such a test for short-term runs in that horizontal boundary layer effects may be rather too crudely represented with the 400 m \times 400 m grid size adopted. A course representation of the boundary layer could possibly result in an underestimate of velocities close to the river mouth and hence an overestimate of the actual time for the plume to reach free-stream conditions.

Two locations were chosen, one, three grid distances WNW of the King River inflow location (just out of the embayment configuration of Lettes Bay) and the other, three grid distances SE of the null cell representing Cat Island. These locations were chosen to capture the two

predominant drift paths as shown by velocity vector plots, one down the eastern side of the northern harbour and the other towards the entrance channel past Yellow Bluff.

A run was set up to examine the output over the same periods as in the previous analysis (commencing the 4^{th} March and the 19^{th} March) with point source inputs (flows and concentrations) giving typical copper loads of 150 kg/hr at each location for four hours (0400 to 0800 hrs) on each of the above designated days.

Period 0500 hrs 4th March to 1100 hrs 5th March with NE wind

For this 30 hr period, the velocity vectors (fig 3.45a) show almost a continuous outflow as a result of wind direction and periods of tidal inflow being much smaller than tidal outflows (see fig 3.42).

Figure 3.45 gives the resulting plume migration and dispersion over the period at 2 hourly intervals for the two plumes in the surface layer.

The view sequence is interesting since it clearly shows the two plumes tracking separately down their respective sides of the northern harbour while simultaneously undergoing a diffusive process due to turbulence. The one to the east tracks past Yellow Bluff while the one to the west tracks past King Point and the plumes barely coalesce over the duration of the period. The test gives a good understanding of typical distances travelled and time taken for the dispersal of a plume from an isolated point source.

Resulting concentrations for total copper are about 1 μ M which, pre-empting section 5.4, correspond to a free copper ion concentration or 'toxic' copper concentration of about 10⁻⁷ M. Such concentrations (which are well above the nominal toxic threshold value of 3×10^{-9} M) are seen to persist in the region off Yellow Bluff for a period approaching 12 hours for the input pulse of 150 kg/hr over 4 hours. Similar levels of copper concentration were found with the first analysis above, that with the NE wind. It should be remembered however, that these are conservative tracer tests without any chemistry activated.

Period 0500 hrs 19th March to 1100 hrs 20th March with SW wind

For this 30 hour period, the wind is a south-westerly to begin (for 3 to 4 hours) after which it swings to become a westerly and at times a north-westerly. Under these winds and with a similar tidal forcing to that of the earlier run, the resulting velocity vectors (fig 3.46a) show a very different picture. They remain very weak over most of the period with the plume being held-up into the north-east corner of the northern harbour.

Figure 3.46 shows the relatively small amount of plume migration and dispersion over the period at 2 hourly intervals for the two plumes. Again the resulting concentrations are given for the surface layer and the two plumes barely coalesce over the 30 hour period.

Resulting concentrations for total copper are again about 1 μ M with peak concentrations being maintained at about 2 μ M over the latter 15 hours. This shows about a 10-fold dilution over peak initial concentrations in a weak advective field.

3.8.3 Indicative concentrations in the region of Yellow Bluff

In regard to resulting copper concentrations in the vicinity of Yellow Bluff, a region with potential for fish farming and hence of special interest, reference is made to section 5 Model Results and in particular figure 5.3 which compares the time series of copper concentrations at nearby Station 6 for all scenarios run.

Again pre-empting section 5.4, a typical resulting total copper concentration for the untreated conservative run of 20 μ g/L, (0.32 μ M) translates to a *toxic* copper concentration of about 3 \times

 10^{-8} M which is an order of magnitude higher than the nominal threshold value indicative of toxic conditions.

Figure 5.3 is then of interest as it shows the very considerable reduction in copper concentrations for the two 'treated' scenarios which will largely achieve the desired reduction in 'toxic' copper concentrations.

4 The chemistry of Macquarie Harbour

4.1 Overview

The chemistry of Macquarie Harbour is complex and unknown in its entirety. An informative earlier review of the chemistry of the harbour can be found in Carpenter et al (1991).

In order to quantify the chemistry, sufficient to meet the objectives of the study as set out in section 2 (broadly to quantify the Cu speciation) the approach has been to represent the major speciation processes with conceptual models, these being adsorption to surfaces and complexation with organic matter.

The King River discharge to Macquarie Harbour contains high levels of Cu. As is common for acid mine drainage, the discharge also contains high levels of other metals Fe, Al and Mn all strongly correlated with and in concentrations of a similar order of magnitude to those of Cu.

The chemical component of the overall model of Macquarie Harbour is therefore required to model the dissolved Cu exported down the King River and to react it with surrounding compounds to arrive at the distribution between adsorbed copper, organic complexed copper and inorganic copper. This last component is assumed to contain the toxic fraction (the free uncomplexed Cu^{2+} ion) in line with the 'free ion model' commonly used to explain toxicity in water (Campbell 1995).

Key processes for King River waters entering Macquarie Harbour are as follows.

- 1. Fe, Al and Mn will precipitate hydrous oxides and/or flocculate as the pH and ionic strength increases on mixing with the more saline waters of the harbour.
- 2. With increases in pH, Cu will adsorb onto the oxide surfaces and hence be involved in the precipitation/flocculation processes.
- 3. Previous studies indicate that some of the copper is strongly complexed by dissolved organic ligands (Carpenter et al 1991, Batley et al 1995a, Teesdale et al 1996).

As earlier stated, the USA EPA chemical thermodynamic equilibrium model MINTEQA2 has been adopted to simulate these processes. Details of the modelling procedure, essentially the application of MINTEQA2 to Macquarie Harbour, are given in the following sections.

At the outset it was recognised that a chemical thermodynamic equilibrium model was being used in a non-equilibrium situation. The rationale to proceed was that the kinetics of the chemical model would produce rapid equilibria with respect to the hydrodynamic time scale such that the hydrodynamics would always be distributing (transporting) newly modified chemical constituents within the three-dimensional domain of the harbour. This would constitute a series of equilibrium states at small time steps moving towards an equilibrium state of a longer characteristic time. In retrospect, rapid aqueous processes would seem to have been captured but not the longer-term processes represented by the interaction between the sediments and the overlying harbour waters. Such processes have not been addressed in this work.

4.2 The nature of the copper inputs to the harbour

Concentrations of filterable copper discharged from the lower King River were highly variable (0.1 to 9 mg/L) during the intensive monitoring period (fig 4.0), and showed a complex relationship with King River hydrology. As is common for acid mine drainage, the river also contains high concentrations of other metals: Al, Fe and Mn. Their concentrations were of a similar order of magnitude to Cu and were highly correlated with Cu concentrations.



Figure 4.0 Variation of filterable Cu, Fe, Al, and Mn in the lower King River from December 1994 to March 1995

pH is the main variable controlling the fate of this copper, and hence the type of transformations it may undergo when discharged to the harbour. pH was not reported for the intensive sampling period of the King River, but measurements of pH made at other times during mine operation (McQuade et al 1995) indicate that pH was low enough to ensure all Cu is in the dissolved form during its passage down the river (table 4.1). Note that after mine closure, pH is likely to be lower than values reported in table 4.1, because the river is no longer buffered by the 'alkaline' tailings discharge (Koehnken 1996).

	Queen River	King River	King River
	Queenstown	Teepookana	Delta
рН	3.8 (2.8–4.7)	4.7 (3.8–6.2)	4.6 (3.0–4.7)
filterable Cu	14 (2.1–45)	0.6 (0.04–2.2)	0.93 (0.08–8.2)
filterable Fe	57 (6.6–156)	1.6 (0.05–5.7)	2.44 (0.05–15)

Table 4.1 Mean and (range) of pH, Cu and Fe concentrations in the Queen and King Rivers during mine operation (from McQuade et al 1995, p37). Units for Cu and Fe are mg/L.

In contrast, at these pH, Fe (II) will be oxidised to Fe(III) and precipitate as colloidal iron oxide. Films of the orange, amorphous hydrated iron oxide are encountered on shingle at Queenstown, where the pH of the acid mine drainage is raised sufficiently by freshwater inflows.

4.3 The formation of the adsorbing surface in Macquarie Harbour

4.3.1 Chemical processes forming adsorbing surfaces

Current wisdom (reviewed in Batley et al 1995a) would predict that the iron colloids in the river would flocculate as the salinity increases in the delta region, probably in the region 0-3 psu. As the salinity increases, the pH will also increase to where Cu will adsorb onto the hydrated iron oxide. This is indeed observed in laboratory experiments on mixtures of King River and Macquarie Harbour water (O'Grady & Featherstone 1995). The process is illustrated in figure 4.1 for a range of hydrated iron oxide concentrations using procedures outlined later.

The precipitation, flocculation and adsorption processes are complicated somewhat by the presence of significant amounts of the other metals Al and Mn. Both Al and Mn are expected to be in the dissolved state at the pH encountered in the King River. The solubility product of aluminium hydroxide is not exceeded in the river, but Al is expected to precipitate and flocculate at pH 5.5-6.5, which is encountered in the King River delta. The Al(OH)₃ soformed, either as discrete particles or in association with other suspended particulate matter (SPM) can also adsorb Cu.

The precipitation of manganese as insoluble oxides is more difficult to predict. Manganese in the acid mine drainage is expected to be in the dissolved Mn (II) oxidation state, because Mn(II) is thermodynamically stable and soluble under the low pH, low carbonate conditions (Garrels & Christ 1965). In the King River, thermodynamic calculations indicate that higher oxidation states are more stable as the pH increases to \sim 3–4, and insoluble Mn (III, IV) oxides should form. (These oxides are typically given the formula MnO_x, to reflect the mixed III + IV oxidation state.) So from thermodynamic reasoning, insoluble manganese oxides should precipitate in the King River.

However, whether or not a thermodynamically stable phase forms also depends on kinetic factors. In this case, rates of oxidation of Mn (II) to hydrous Mn (III, IV) oxides would be extremely slow at the low pH of the King River and its delta (estimated half lives would be many years—Davison 1993). The high correlation between filterable Mn and Cu concentrations in the King River does not necessarily reflect an actual association, such as adsorption, but could be expected because dilution down the river will affect each dissolved component equally. (Note that there is not such a good correlation with Fe, but this may reflect the possibility that Fe is being removed by settling onto the river bed).



Figure 4.1 Adsorption of Cu on 0.1 to 5 mg/L hydrated iron oxide. Salinity = 20 psu, total Cu (TCu) = 50 μ g/L, pH = 8.2.

Mn (II) oxidation and precipitation would proceed at moderate rates at the higher pH encountered in more saline waters in the harbour proper—with half lives typically of days to months (Wilson 1980, Pankow & Morgan 1981, Stumm & Morgan 1981, Davison 1993). Therefore Mn is not expected to precipitate immediately in the King River or its delta, but to precipitate subsequently in Macquarie Harbour, possibly through the mediation of bacteriological activity.

In addition to the complexity of the metal oxide adsorbates formed in the harbour, it is well known that natural organic matter (DOM) will adsorb onto metal oxides. There is sufficient organic matter present in the harbour to form a significant coating on metal oxide films.

In summary, when King River waters are discharged into the harbour, in the low salinity region, hydrated ferric oxide is likely to be flocculated and $Al(OH)_3$ precipitated. It is assumed that clay and silt particles can be neglected as a separate adsorbing phase, because they should be coated by the other metal oxide phases. In the main body of the harbour, however, the nature of the adsorbent material may change with precipitation of MnO_x and adsorption of organic material. Therefore, the solid phases formed in the King River delta and Macquarie Harbour are complex and probably changing in adsorptive characteristics with distance from the King River mouth.

4.3.2 Calculation of concentrations of adsorbing phase

At the present time, no studies on the nature and amounts of adsorbing phases in the harbour have been carried out. From the forgoing, we assume that the adsorbing phase is a mixture of iron, aluminium and manganese oxides. In the following, we estimate the amount of adsorbing phase from information on concentrations of Fe, Al and Mn and published data on the concentration of adsorbing sites on surfaces of their oxides. We estimate the concentration of the adsorbing phase by reviewing the information from three studies; two on the harbour (Teesdale et al 1996, Stauber et al 1996) and one on the King River (Koehnken 1996).

Fe and Mn have been measured by Teesdale et al (1996) at 10 sites in the harbour. Note that the relative importance of Fe and Mn in the main harbour can be assessed from their data by comparing the ratio of 'total' Fe or Mn concentration to 'total' copper concentration (concentration in moles per litre). Their data can be used directly because they analysed their unfiltered samples after weak acid (pH 2) extraction, which will only dissolve amorphous metal oxides, and not Fe and Mn bound in lattices of minerals. (It is the amorphous material that will be the adsorbing phase.) The ratios indicate that Fe is more important than Mn, especially in the surface waters of the northern harbour, because there are sufficient surface complexing sites available for Cu on Fe (oxides) compared to Mn (oxides).

The study by Teesdale et al (1996) did not measure Al. This was measured in Project 8 (Toxicity of Macquarie Harbour waters), but only as filterable concentrations (Stauber et al 1996). In this case, filterable Al concentrations were greater than either filterable Mn or Fe, and Al will be the dominant particulate-forming phase in filtered samples (table 4.3).

Table 4.2 Statistics for the mole ratios of total copper, iron and manganese in Macquarie Harbour(calculated from Teesdale et al 1996, their table 3.1, 3.3)

Concentration ratios (moles/litre)	Range	Mean	Mean (surface Northern Harbour)
Ratio of total metal to copper			
Fe /Cu	4–27	13.1	7.2
Mn/Cu	0.6–6.5	2.8	1.5
Ratio of surface sites to copper ¹			
Fe-sites/Cu	1.1–5.6	2.7	1.48
Mn-sites/Cu	0.2–2.7	0.94	0.52

1 Based on data from Morel & Hering (1993), Fu et al (1991).

Table 4.3 Molar ratios of filterable copper, iron, manganese and aluminium in Macquarie Harbour (calculated from Stauber et al 1996 their table 4.1)

Concentration ratios (moles/litre)	Range	Mean	
Ratio of total metal to copper			
Fe /Cu	1.9–2.8	2.4	
Mn/Cu	1.8–2.8	2.5	
Al/Cu	9.1–17	11	
Ratio of surface sites to copper ¹			
Mn-sites/Cu	0.6–0.9	0.8	
Fe-sites/Cu	0.4–0.6	0.5	
Al-sites/Cu	1.7–.3	2.2	

1 Based on data from Morel & Hering (1993), Fu et al (1991) and assuming that $Al(OH)_3$ has the same site density as hydrated iron oxide.

Information from the King River is also based on filterable concentrations (table 4.4, fig 4.2). These show that the ratio of surface-forming metal (Fe, Mn, Al) concentrations to copper concentrations are highly variable. The ratio Mn/Cu is consistent with what is observed in the harbour. This is expected because both metals should be in the solution phase in the river. The Fe/Cu ratio is very low compared to that observed in the harbour (compare table 4.2 and table 4.4). However, filterable Fe may be a poor estimate of total hydrated iron oxide discharged to the harbour because most of the iron in the river should have precipitated out and hence be non-filterable.

Other data gives some clues as to the likely maximum ratio of Fe to Cu. Further upstream at a site just below Queenstown during the period before mine closure, the pH and travel time are sufficiently low that most Fe is still in a filterable form. Therefore measurements of filterable

Fe will be probably close to total Fe (table 4.1). Here Fe/Cu molar ratios were approximately 5 and the average molar concentration ratio of Al/Cu is 4.3.



Figure 4.2 Variation in filterable (Fe+Mn+Al)/Cu molar concentration ratios in the lower King River

near its mouth, together with	r its mouth, together with their ratios to copper concentration			, , , , , , , , , , , , , , , , , , ,
	Cu	Fe	Mn	AI
Mean concentration	27	12	43	125

0.75-125

1.2

0-19.6

2.4-235

1.8

0-29

0-726

4.3

0-20

0-140

1

Range

Range

Mean Me/Cu

Table 4.4 Average concentrations (µM) of filterable Cu, Fe, Mn, AI concentrations in the King River

To calculate the total amount of adsorbing phase, we combined the best estimates of Fe, Al and Mn reviewed above. The best information on Mn and Al is that from the King River monitoring, so Mn and Al concentrations were taken directly from the measured concentrations in the lower King River or from the average ratio between their concentrations (table 4.3). As described above, the filterable Fe concentration in the lower King River may not be a good estimate of the Fe available to form adsorbing surfaces. Therefore concentrations were estimated from Fe/Cu molar ratios using the following reasoning. It is likely that this ratio is greater than that found for filterable Fe and Cu in the lower King River (average = 1.2), but less than the ratio of 5 found near Queenstown, due to precipitation in the King River system. We adopted 2.8 measured by Teesdale et al (1996) from table 4.2, but recognise that this is subject to a degree of uncertainty because it is observed during a one-off survey.

The average ratio of the adsorbing phase concentration to Cu concentration is therefore = [Mn] + [A1] + [Fe] = 1.8 + 4.3 + 2.8 = 9.9 or ~10. To summarise, on average, adsorbing phase concentrations were approximately 10 times copper concentrations during the period December 1994 to March 1995.

4.3.3 Modelling copper adsorption

Copper adsorption was modelled using a surface phase with the same characteristics as hydrated ferric oxide. For convenience, this phase is referred to as HFO (Dzombak & Morel 1990).

The HFO adsorption model was chosen for the following reasons:

- It is a major phase in Macquarie Harbour.
- The hydrated Fe oxide (HFO) surface adsorption model found in the MINTEQA2 computer speciation program is the most comprehensive database available for surface adsorption and is widely applicable, even to the relatively high Cu/Fe ratios found in the Macquarie Harbour.
- Given the limits of our understanding of adsorption in the Macquarie Harbour system, it is more efficient to explore options and scenarios with the most well-tried adsorption program, which is known to be robust over a wide range of conditions.
- Dzombak and Morel (1990) found that the HFO database coupled with the double-layer adsorption model now incorporated in MINTEQA2 works well for many situations, and seems to perform as well as the more sophisticated models, such as the triple layer model.
- Adsorption of any trace metal on commonly encountered solid phases (Al₂O₃, HFO, MnO_x, SiO₂) show general similarity, so even though the iron hydrous oxide is not the sole adsorbing surface, it is likely to respond in the same general way to the 'as yet unknown' surface, that is, adsorption increasing from 0 to 100% over the pH range 4 to 7. It is expected that the model adopted will give reasonable predictions on relative changes in adsorptive behaviour in the harbour. We believe that this is the best that can be done until direct measurements are made on the adsorption characteristics of the particulate material (both settleable and colloidal) in the harbour.

For the modelling runs on Cu adsorption in the harbour, we assumed that the HFO concentration = [Mn] + [Al] + [Fe]. The range of this 'quasi-HFO' concentration likely to be encountered in the harbour was 0–5 mg/L. (In practice we created a 'look-up table' using 0, 0.1, 0.2, 0.5, 1, 2 and 5 mg/L HFO.)

The surface parameters used were (Morel & Hering 1993, p543):

	Molecular Weight	1 mole/90 g of HFO
	Specific surface area	600m ² /g
	2 surface sites, one weak (=Fe _w OH) and one strong	$(=Fe_sOH)$ with concentrations:
	[≡Fe _w OH] _{tot}	= 0.2 moles/mole HFO
	[≡Fe _s OH] _{tot}	= 0.005 moles/mole HFO
In MIN	TEQA2 we nominate:	

•	concentration of surface adsorbing material in	g/L
•	specific surface area in	m^2/g
•	concentration of sites in	moles/L
•	ADS1TYPE1	= strong site
•	ADS1TYPE2	= weak site

And to specify site concentration in units of moles/g:

[ADS1TYPE1]	= 0.005/90 moles/g	$= 5.56 \text{ x } 10^{-5} \text{ moles/g}$
[ADS1TYPE2]	= 0.2/90 moles/g	$= 2.22 \text{ x } 10^{-3} \text{ moles/g}$

4.4 Organic complexation of copper in Macquarie Harbour

4.4.1 Studies on complexation in the harbour

In many aquatic systems, dissolved copper speciation tends to be dominated by organic complexes (Batley et al 1995a). Organic complexation may be important in Macquarie Harbour, because of studies reporting copper complexation (Carpenter et al 1991) and because of the relatively high concentration of organic matter in the harbour (table 4.5).

Table 4.5 Concentrations of DOC (mg/L) in the harbour

Reference	Gordon	Harbour surface	Harbour bottom
Carpenter et al (1991)	5.4	1–3.4	
Batley et al (1995)		0.3–10	0–4.4

Carpenter et al (1991) measured the copper complexing capacity (CuCC) with a technique which measures very strong complexes with copper, specifically complexes with conditional stability constants (K) of more than 10^{11} . They found a relationship between CuCC and dissolved organic carbon (DOC), where 5 mg/L of DOC has a CuCC of about 130 nM. They found that the complexation capacity of organic matter in the Macquarie harbour was exceeded by the copper concentration. At the time of their study, copper concentration were considerably lower (total copper was 4–11 µg/L) than usually found in the DELM study. Their technique for measuring CuCC does not take into account the copper complexation capacity of weaker organic complexes (Batley et al 1995a).

In contrast with the study by Carpenter et al (1991), Apte et al (1996) found no relationship between measured copper complexing capacity and DOC concentrations in Macquarie Harbour. Teesdale et al (1996) assessed the copper complexing capacity of complexes with conditional stability constants in the range 10^9-10^{11} . At the two sites they examined, the complexing capacity was exceeded in the surface waters and in the bottom water at one of the sites. There was excess capacity in the bottom waters at the other site.

It may also be possible that the measurement techniques used to date have incorrectly attributed some of the surface adsorption to strong organic complexation, so that the importance of organic complexation has been overestimated.

Given the scarcity of information, a number of approaches to organic complexation were considered. Trials were carried out on various organic complexing models.

Fulvic acids

The effect of complexation by fulvic acids was examined. This seemed appropriate considering the nature of the freshwater inputs and the resulting strong colour and high DOM content of the harbour waters. This model is based on the work of Dobbs et al (1989a,b) which treats dissolved organic matter as a complex material consisting of many different types of monoprotic acid sites. The concentration of these ligand sites is normally distributed with respect to their log stability constant (log K) values for protons or metals. These log K values have been determined for various metals with dissolved organic matter from the Suwannee River (Perdue et al 1984, Susetyo et al 1991).

While organic complexation had a significant effect on copper speciation in freshwater, it had a negligible effect in seawaters, particularly because of the competition with Ca^{2+} and Mg^{2+} and the relatively low stability constants between Cu and DOM. The mean log K is ~7 for formation of these Cu-DOM complexes. Therefore fulvic acids, expected in the Gordon and King River drainage, had negligible effects on copper speciation in seawater at salinities of 10–35 psu. Stability constants for Cu have to be much larger than those reported for fulvic acid to produce significant organic complexation.

The strength of the stability constant

The effect of increasing values for stability constants was examined by varying thermodynamic pK values from 7 to 10 (table 4.6). While this procedure is somewhat artificial because there is no competition with other metals, and no adsorption reactions, it does show the sensitivity of Cu organic complexation to log K values.

Table 4.6 Complexed copper concentrations (%) with 1:1 DOM complexes in seawater (35 psu, pH 8.3). Cu = 8×10^{-6} M, DOM = 26×10^{-6} M.

log K	% complexed
7	6.1
8	37.1
9	83.1
10	97.9

Information from other studies

There is a great deal of controversy about the likely value of stability constants for metalnatural organic complexes in the literature (van den Berg 1993, Batley et al 1995a). Conditional stability constants used or measured in various studies range from 10^7 to 10^{16} . Current wisdom suggests strong complexation by some organic ligands with thermodynamic stability constants for Cu-ligand complex formation of $\sim 10^{10} - 10^{13}$ are likely in estuarine and marine coastal waters (S Apte, CSIRO, Centre of Advanced Analytical Chemistry, pers comm). These strong complexing agents are often attributed to algal exudates. S Apte (CSIRO, Centre for Advanced Analytical Chemistry, pers comm), on the basis of his experience studying organic complexation in estuaries, recommended that organic complexation might be modelled generally by assuming equimolar concentrations of 2 ligands with conditional stability constants of 10^9 and 10^{12} . For conditional stability constant of 10^{12} , this approximates to a thermodynamic stability constant of between $10^{13.1} - 10^{13.6}$ for complexation between Cu²⁺. depending on assumptions made on the ligand charge. As described above, both Carpenter et al (1991) and Teesdale et al (1996) found that the copper complexing capacity is almost always less than the copper concentrations. Under these conditions, the complexation by ligands with conditional stability constants of 10^9 is negligible.

4.4.2 Modelling copper complexation by organic matter

On the basis of the above information, a simple approach consistent with the current state of knowledge was chosen. We assumed a ligand with properties similar to NTA, a tridentate acetate-type ligand with a copper-NTA thermodynamic stability constant of $10^{13.3}$ (which translates to a conditional stability constant of about 10^{11} – 10^{12}). Note that at the pH encountered in the King River, this ligand is only partly dissociated and it does not complex copper until pH is >5.

At pH above 6, the predicted concentrations of organically complexed copper are almost identical for the NTA-type ligand and for the ligands recommended by Apte above. The sensitivity of copper speciation to the assumed charge on this ligand was tested by varying the charge from -1 to -3. There was an insignificant effect on the overall copper speciation.

In the model ligand concentrations were estimated on the basis of the relationship between CuCC and dissolved organic carbon (DOC) found by Carpenter et al (1991). DOC concentration in the Gordon River was assumed to be 10 mg/L, in line with measurements by Batley et al (1995b). DOC concentration was also assumed to be 10 mg/L in the King River (D Klessa *eriss*, pers comm) and 1 mg/L in the saline end-member.

4.5 Inorganic speciation of copper

4.5.1 The chemistry of copper

The balance of Cu in the harbour that is not complexed by organics, or adsorbed onto particulate matter, is predominantly dissolved Cu^{2+} , $\text{Cu}(\text{OH})_2^{0}$, CuCO_3^{0} , $\text{Cu}\text{HCO}_3^{+}$, (fig 4.3) and small amounts of CuSO_4^{0} and CuCl^+ . Figure 4.3 shows the calculated speciation for a single situation with a relatively high copper concentration and low concentrations of HFO and organic matter.

The question of precipitation of insoluble copper compounds was addressed. Calculations performed with MINTEQA2 at pH and salinity found in the Macquarie Harbour show that of the various insoluble copper compounds that have been found in other aquatic systems, CuO is the most insoluble copper phase. The copper concentrations needed to be exceeded for CuO to precipitate were then calculated. In these calculations, temperature, pH and salinity variation in the harbour were taken into account. Temperature and pH have a large influence on CuO solubility, but salinity variation has little effect. Cu adsorption or complexation was not taken into account, so the calculations are conservative, ie, they will overestimate the likelihood of CuO formation.

In the main body of the harbour, these calculated 'saturation' or 'equilibrium' concentrations of total dissolved Cu^{2+} are always much higher than our best measure of dissolved Cu (Cu_{ASV}) throughout the harbour, so the harbour is not supersaturated with respect to CuO, and this phase will not be controlling copper concentrations and fate.

The likelihood of CuO precipitation near the King River mouth was examined, where high dissolved concentrations are found from time to time. Our calculations show that CuO is most insoluble at high pH and high temperatures. For example, at pH 8 and 20°C, the equilibrium concentration of total dissolved copper is predicted to be 80 μ g/L, whereas at pH 7 and 10°C, equilibrium total dissolved copper concentration is 635 μ g/L. While high concentrations are often found near the King River mouth, there are a number of factors which argue against CuO precipitation there. Firstly, high concentrations of Cu are accompanied by low pH conditions, which means CuO will not precipitate. Secondly, as the pH increases with mixing between the King and harbour waters in the delta, dissolved Cu is removed by adsorption and complexation. Therefore it is also unlikely that CuO precipitates near the King River mouth.

4.5.2 Modelling inorganic speciation

The concentration of inorganic ions was assumed to be the same as in seawater diluted by lowionic-strength freshwater. MINTEQA2 contains a database of thermodynamic complexation with most of the important inorganic species. This was used unamended.



Figure 4.3 Copper speciation in Macquarie Harbour for $[TCu] = 7.9 \times 10^{-7} \text{ M} (50 \,\mu\text{g/L}), [DOM] = 1.3 \times 10^{-7} \text{ M} (5 \,\text{mg/L}), [HFO] = 1 \,\text{mg/L}.$ Cu inorganic = Cu²⁺ + Cu(OH)₂ + CuHCO₃⁺ + CuCO₃.

4.6 pH of harbour waters

The relatively low pH in the higher salinity waters was surprising, because pH typical of seawater (about 8.2–8.3) was expected. The DELM findings have been confirmed in other studies. Carpenter et al (1991) and Batley et al (1995a) found similarly low pH. One explanation is that pH has been lowered by the acid inputs, even in the saline waters. In the case of the deeper saline waters, where there is little input by the fresh water inflows, it is assumed that the acid inputs have come from oxidation of sulphidic minerals or acid volatile sulphide. pH/salinity plots for the DELM data show considerable scatter, and some hydrocasts may have suffered calibration problems.

We assumed a simple linear relationship between pH and salinity for the harbour consistent with the majority of the DELM data (fig 4.4). One problem with this approach is that it neglects acid inputs from the King River delta (Teesdale et al 1996), but presently it is not known how to estimate these.



Figure 4.4 pH-salinity relationship used in model

4.7 Copper toxicity

Copper toxicity in water depends on the form of the copper present. The dissolved, free, uncomplexed Cu^{2+} or $Cu(H_2O)_6^{2+}$ ion is known to be toxic. Many reactions in the aquatic environment result in dissolved copper being converted to more, less or non-toxic forms. Organic complexation is a good example of this, complexation by some organic compounds may reduce copper toxicity while others enhance it. At present, the most common model of copper toxicity is the Free Ion Model (Campbell 1995), which attributes copper toxicity to the concentration of its free ion $(Cu^{2+} \text{ or } Cu(H_2O)_6^{2+})$, and there are many studies which show that this model is appropriate. Other studies have shown that the measurement of the ASV-labile fraction is a more appropriate estimate of the toxic fraction in some cases. Yet other studies have shown that a particular Cu-organic complex controls toxicity.

The information on Macquarie Harbour was reviewed to see which toxicity model was appropriate to link to the hydrodynamic-chemical model. In their studies on Macquarie Harbour, Stauber et al (1996) found a significant relationship ($r^2 = 0.51$) between ASV-labile copper and inhibition of enzyme activity in the marine alga *Dunaleilla tertiolecta*. However, for the other tests, there was no relationship between ASV-labile copper and algal growth, amphipod survival, or juvenile flounder survival, osmoregulation and copper accumulation in flounder.

It seems that the ASV-labile Cu model of copper bioavailability is not the most appropriate to the Macquarie Harbour waters. Instead, the more common Free Ion Model was chosen.

Concentrations of free copper ion which are toxic to aquatic organisms were calculated directly from studies of Stauber et al (1996). The most sensitive test was the inhibition of growth of the marine alga *Nitzschia closterium*. Their results showed that total copper concentrations of 42 and 52 μ g/L produced a significant decrease in growth of these algae in two samples taken

from Macquarie Harbour. The toxicity tests did not measure the parameters used in the chemical model of the harbour so these were estimated as follows. Concentrations of free Cu²⁺ at these total concentrations were calculated assuming a pH of 8.1 (the pH ranged from 7.9–8.2 during the tests), a total surface oxide/TCu concentration ratio of 15.9 (table 4.3), and DOM = 10 mg/L (section 4.4.2). Under these conditions, the corresponding free copper ion concentration was about 3 x 10⁻⁹ M.

In the chemical model for the harbour, the free copper ion concentration for all cells has been calculated. The water is assumed to be potentially toxic to aquatic organisms when the free Cu^{2+} concentration exceeds 3 x 10⁻⁹ M.

The variation of free Cu^{2+} with changing pH, HFO, DOM and total copper concentration is illustrated for a number of different conditions in figures 4.3 and 4.5.

4.8 Results of MINTEQA2 modelling

Results of deliberations on the chemistry of Macquarie Harbour were brought together in the use of the MINTEQA2 model to provide 'look-up' tables of % adsorbed and % complexed total Cu for the full range of conditions expected within the harbour and parameterised by concentrations of Cu, Fe, DOC and pH. Concentration of the free copper ions (toxic Cu) was also uniquely determined by the parameterisation.

As previewed in section 2, the graphical representation of the 'look-up' tables are given in figures 4.6a to 4.6d.

4.9 Limitations of the chemical model

The model was calibrated against total copper. It was unclear how to interpret the ASV-labile copper in terms of the chemical modelling. Generally, adsorption and desorption is a slow process, so that adsorbed Cu is not expected to be ASV-labile. Stauber et al (1996) offer the possibility that adsorbed Cu is at least partially labile, and while this possibility is very tentative, it does raise the need to determine the nature of ASV-labile Cu before using it to validate the model. This is particularly true because the model has shown that copper speciation is very dependent on the concentrations of Fe, Mn, Al and DOM, the first three of which at least are highly variable.

Our study has demonstrated that the Macquarie Harbour system is very complex to model, because of the variability of inputs (both Cu and other components that affect its fate), the uncertain nature of the adsorbing and complexing agents, and the uncertain nature of the toxic fraction. Despite these difficulties, modelling has been shown to be worth pursuing, and substantial improvements could be achieved in predicting toxic concentrations if measurements were made of adsorption and complexation characteristics (both stability constants and concentrations) in the harbour along with further algal toxicity tests. This is outlined in the following.

The adsorption surface in Macquarie Harbour is likely to be different from the one used in the model. It is unlikely that adsorption surfaces can be treated as simple mixtures of Mn-OH, Al-OH and Fe-OH. Even if this could be achieved, there is insufficient information on these other phases to incorporate them into the MINTEQA2 model. Therefore, there is little point in pursuing improvements to the adsorption characteristics of the model until adsorption isotherms are measured directly using Macquarie Harbour water. This would yield appropriate empirical constants that could be related to the Fe, Mn and Al content of the particulate matter.



Figure 4.5 Variation in free Cu²⁺ concentrations (M) with (**A**) HFO, (**B**) DOM and (**C**) Total Cu. (Units in legend to **C** are μg/L)

A HFO=0.1-5 mg/L, TCu=50 μg/L, DOM=5 mg/L **B** HFO=0 mg/L,TCu=50 μg/L, DOM=0-10 mg/L **C** HFO=5 mg/L, TCu=2-500 μg/L. DOM=5 mg/L There are even greater uncertainties in respect to modelling organic complexation given:

- the uncertainties about appropriate stability constants to select for Macquarie Harbour organic matter;
- the possible overestimate of the importance of copper complexation because of interference from adsorption during complexation measurements made in reported studies;
- the sparse information on DOC concentrations in the harbour;
- the uncertainty over DOC/ligand relationships;
- the lack of direct measurements of ligand concentrations.

However, some uncertainty is usual in describing and modelling organic complexing in coastal waters in other parts of the world (van den Berg 1993).

If we adopt stability constants for fulvic acid complexes with copper as reported in the literature from other parts of the world, then these would be too weak to be important in Macquarie Harbour. In contrast to the relatively weak fulvic acid complexes, strong organic complexation has been reported for copper species in estuarine and marine waters in some overseas studies. The source of this matter is likely to be algal exudates. The concentration of these exudates is quite low and copper concentrations reported in these are also very low resulting in a high proportion of copper being complexed. Again in contrast, the much higher copper concentrations in Macquarie Harbour and the unfavourable conditions for algal growth (highly coloured water) would argue against a complexation mechanism with algal exudates being important here.

It is possible that measurements of complexation carried out to date have suffered interference by adsorption processes. Direct measurement of strong organic complexing is needed not only to obtain the appropriate quantitative information, but also to understand what it derives from. These measurements will need to be conducted with a Cu ion selective electrode and the appropriate manipulations of the sample using UV digestion to destroy organic matter and ultrafiltration to remove colloidal material.

Further work on inhibition of enzyme activity in the marine alga *Dunaleilla tertiolecta* and the inhibition of growth of the marine alga *Nitzschia closterium* is recommended along with appropriate chemical measurements. These tests offer the most promising and exciting means to directly identify the toxic species and their concentrations. Two copper fractions have been identified so far (Stauber et al 1996). There is a significant relationship between ASV-labile Cu and bioavailability measured by the inhibition of enzyme activity in *Dunaleilla tertiolecta*. However, the proposed mechanism for this toxic response is novel, and calls into question the intuitive interpretation that adsorbed Cu is not ASV-labile. Further toxicity tests, carried out with the appropriate chemical measurements described above, offer the possibility of interpreting the nature of the ASV-labile fraction, as well as the other toxic fraction.

In respect to inorganic speciation, improvements to the modelling could be made if alkalinity in the Gordon River inputs were known. This is critical for modelling the pH changes around the King River delta.

4.10 Test for copper movement in the water column

Prior to considering the model's performance on production runs over the adopted 4½ month test period, it is illustrative to consider the basic movement of copper and to gain some understanding of the time and space scales over which loadings from the King River are distributed and dissipated within the water column.

The period and loading for the copper deposition test given in section 3 (fig 3.33) is again the basis for the following result sequence. In section 3, cumulative copper deposition plots (fig 3.34) were given over a period of about 24 hours following a peak loading.

In the related set of plots (fig 4.7a to 4.7d) the concentrations in the water column are given at 12 hourly intervals over about 7 days commencing at 0600 hrs on the 27^{th} January 1995 almost $3\frac{1}{2}$ days before the peak. These results clearly show the rapid increase and decrease of copper concentrations in the water column. First they exhibit a fall-off in water column concentrations of copper from an earlier loading event then peak concentrations soon after the peak loading (within 6 to 12 hours) followed by a decline to conditions before the peak loading within $3\frac{1}{2}$ days with most of the copper apparently falling-out via the adsorption and colloidal settling process.

5 Model results

5.1 Preamble

The accompanying plots address the following comparative features arising from the integrated hydrodynamic and chemical modelling of Macquarie Harbour.

- A comparison between the measured behaviour and model predicted behaviour of copper loadings from the King River discharging to Macquarie Harbour in the test period 1st December 1994 to 13th April 1995.
- Results for two different proposed treatment scenarios (Stock 2 and Stock 3) running over the same period, that is, running with the same underlying hydrodynamics.

For the results presented, the following three mechanisms should be kept in mind:

- the case of conservative copper where copper is transported around Macquarie Harbour as a conservative (non-reacting) tracer;
- the baseline chemistry of adsorption (with fall-out) and complexation as the two chemical processes implemented to capture the essential chemistry of copper speciation for acid drainage from a mine site entering a marine environment via a river discharge also containing dissolved organic matter (as formulated in section 4);
- the release of copper from bottom sediments, a mechanism not included in the modelling process.

In presenting the three-dimensional, time-dependent results of the modelling, three types of plots are used; time-series plots, orthographically projected (vertically and horizontally) shaded contour section plots and profile plots.

Six sets of plots are presented here.

- 1. Time-series plots (6) for all cases over the duration of the test at 6 locations in the northern harbour (along and northward of the Sophia Pt–Liberty Pt transect). (figs 5.1 to 5.6)
- Section plots (10) for total copper (untreated and treated) from about mid-harbour (Hogan Cove–Coal Head transect) northwards commencing on the 31st December 1994 and given at 10-day intervals. (figs 5.7 to 5.16)
- 3. Section plots (10) for toxic copper (untreated and treated) over the same area and at the same times as the total copper plots. (figs 5.17 to 5.26)

- 4. Section plots (2) covering most of the harbour for the conservative run commencing on the 10th January 1995 and given at 20-day intervals. (figs 5.27a and b)
- 5. Profile plots (11) covering 11 of the 'monthly' field stations in the southern harbour (along and southward of the Sophia Pt–Liberty Pt transect) on the 18th to 19th January, 15th February and 22nd to 23rd March 1995 for the conservative run and the baseline chemical model. (figs 5.28 to 5.38)
- 6. Section plots (1) of sediment fall-out close to the mouth of the King River over the full duration of the 4¹/₂ month test period. (fig 5.39)

5.2 Forcing functions and copper loadings

Figures 5abcd give the hydrodynamic forcing over the test period as discussed in section 3; the predicted tide for Pilot Bay, the Cape Sorell wind (factored by $\frac{2}{3}$ rds to be more compatible with wind at Strahan Airport) and the discharges for the King and Gordon Rivers.

Figure 5.0 is a plot of the copper loadings in kg/hr for the three cases being modelled annotated to indicate the times of the 10 total and toxic copper section plots.

- 1. The untreated (as measured) actual discharge into Macquarie Harbour over the test period following mine closure.
- 2. The Stock 2 case (80% treated) and based on Scenarios 8 and 11.
- 3. The Stock 3 case (99% treated) and based on Scenarios 9 and 12.

The latter two scenario pairs were very representative of the treatment conditions required to be modelled and were translated into time-dependent loadings over the full period by assuming a linear variation between the flows representing the power station 'on' and the power station 'off'. Beyond these flow conditions (ie for higher and lower flows) the concentrations were taken to be those for the high and low flow as given. Determining loadings in this way occasionally resulted in Stock 2 and Stock 3 having a slightly higher loading than for the case of measured loadings (untreated) thus giving rise to unexpected results down at the lower concentration end of the comparisons as occasionally observed in the section contour plots for adsorption/complexation in part 4 below.

The total 'mole equivalent' adsorbing surface was determined for each case. For the untreated case, the concentration of the hydrous ferric oxide component was found by taking the molar ratio [hydrous ferric oxide]/[Cu] to be 2.8 while for Stock 2 and Stock 3 the concentration was taken as a constant 0.5 mg/L. The Al and Mn components of the total adsorbing surface were included; as measured for the untreated case (fig 4.0) and as prescribed in the scenarios for Stocks 2 and 3 as follows (all units in mg/L).

Stock 2: low flow—Al (1.35), Mn (3.37); high flow—Al (0.43), Mn (0.27)

Stock 3: low flow—Al (0.45), Mn (3.37); high flow—Al (0.40), Mn (0.27)

Dissolved organic matter (DOM) was brought into the harbour at a constant concentration of 10 mg/L for both the Gordon and the King.

5.3 Time-series plots—All cases

This series of plots represents the most significant set of results for the study since it provides comparison at three levels. First, the comparison is over the period of the intensive 'weekly' monitoring program (a test period spanning in excess of 4 months) and includes the 'weekly' field data taken at 'top', 'mid' and 'bottom' positions within the water column. (Top layer (0 to

2 m), mid layer (20 ppt isohaline taken to be the 4th layer ie 6 to 8 m) and the bottom layer.) Second, the three chemical mechanisms for modelling copper speciation (the conservative case—no active chemistry, adsorption alone and adsorption with competing complexation) are compared. Third, the predictions for the two treated load cases (Stock 2, 80% reduction and Stock 3, 99% reduction) are also presented for comparison.

Figures 5.1 to 5.6 each give the predicted time series of resulting concentrations of total copper over the test period. These are for 6 sites chosen to be representative of the northern harbour on the DELM weekly measurement circuit. First, Stations 2 and 3 being 'near mouth' stations, then Stations 9 and 6 being mid northern harbour, 9 being more to the East and deeper while 6 is more towards Kelly Channel and shallower. Finally Stations 11 and 14 were located on the ends of the Sophia Point (east)–Liberty Point (west) transect respectively. (See figure 5e for mean locations of DELM monitoring stations.) The different traces are the total copper concentrations for 5 different runs comprising untreated and treated sources with chemistry as defined applying. Average values over the test period can be assessed from the time-series traces.

In reading these plots it is important to keep in mind the three-dimensional and time-dependent nature of the model. The plots give the variation of the computed total copper concentrations through the vertical at the positions where measurements were taken (top, mid and bottom). In presenting the results in this way, it is tempting to look for just the self-consistency between the three levels of each sub-plot per station. What needs to be remembered is that the time-series of concentrations is the result of modelling very complex hydrodynamics, transport of four (4) key scalar quantities and the repeated (pseudo-dynamic) application of a complex thermodynamic chemical equilibrium model.

Three immediate observations are as follows.

- The conservative model (blue trace-no adsorption or complexation) would appear as a reasonable representation of the measured harbour response to copper loads particularly at 'mid' depth. Generally, it is higher than the measured copper levels in the top layer (0 to 2 m) and lower in the bottom-most layers but overall (in a depth-averaged sense) it may provide realistic copper fluxes being transported down into the southern harbour. (See the profile results of part 7 below.)
- Comparison of the two cases of adsorption only (orange trace) and adsorption with complexation (green trace) indicates that the complexation effect is minor. (This is probably an indication that insufficient levels of organic material entering the harbour to allow complexation to be a prominent mechanism). Overall, this adsorption-complexation model with fall-out of the adsorbing particles seems to be a reasonable representation of perhaps the major mechanisms determining the fate of copper in Macquarie Harbour.
- Having made the point that resulting traces for both adsorption and adsorption with complexation are similar, close inspection yields an apparent anomaly requiring explanation. For the 6 stations presented, it is true that almost invariably the total copper concentrations are slightly higher for the case of just adsorption (in the mid and bottom layers) compared to the case of adsorption with complexation. This is as expected since, in the case of just adsorption, more of the copper migrates to lower levels in the water column through the adsorbing onto, then settling, of the carrier particles (the flocculated colloidal hydrous metal oxides). Conversely, the expectation is to see slightly higher levels of copper in the top layer for the case where the competing complexation mechanism also acts allowing less copper to take part in the sedimentation process. This expectation is not generally fulfilled at Stations 2 and 3 but it is at the other stations presented (6, 9, 11, 14).

This suggests that it is insufficient to consider just the time-series plots and the variation between them at the three different levels as an indication of the distribution mechanism for copper. Resultant concentrations will indeed be influenced by the general transport in the three-dimensional advective and turbulently diffusive flow field which the model simulates. Further, it must be remembered that the chemistry of the copper speciation (in reality and as represented by MINTEQA2) is just as complex as the hydrodynamics. All these complexities can have bearing, particularly on the top-layer modelled result at Stations 2 and 3 where the trace for adsorption alone is, in the main, unexpectedly just slightly above the trace for combined adsorption and complexation.

• The Stock 2 and Stock 3 cases give much reduced copper concentrations throughout as expected. With resulting total copper concentrations down to around 2 μ g/L (equivalent to a toxic fraction of about 3×10^{-9} M) the waters around Yellow Bluff are seen to seldom exceed potentially 'toxic' conditions for the treated load cases.

5.4 Section contour plots for adsorption/complexation

This series of 10 plots commences at 00:00 hours on the 31 December 1994 (a month into the run since no residual copper was present in the harbour at the beginning of the run) and continues over the duration of the test period with a plot every 10 days as indicated on figure 5.0. The plots cover a wide range of conditions with generally a rapid dispersal of river plumes (2 or 3 days) expected on the basis of earlier interpretation of results discussed in section 3 and section 4. The plots give a clear indication of the resulting transient distribution of copper within Macquarie Harbour for the integrated hydrodynamic and chemical (adsorption and complexation) processes implemented for the untreated (measured) loading and the two treated cases. The plots generally show reduced total copper concentrations corresponding to reduced loadings with smaller plume excursions and reduced maximum values. In general, the maximum values for the three cases are in approximately the same ratio as the loadings applying at and just prior to the time of the plot.

Occasionally (ie on the 10th Jan, 19th Feb and 11th Mar) the loadings for the treated cases have come out higher than for the untreated (measured) case by virtue of the way they have been calculated from flow dependence. This, along with conditions prior to the instants to which the plots pertain, explains any unexpected results within the comparison of the 3 cases.

As noted from the time-series results above, comparison of results from the adsorption and complexation model with field measurements indicate that it is capable of modifying a conservative copper field in a realistic way producing copper concentrations through the water column which are very much the appropriate levels in the northern harbour (north of the Sophia Pt–Liberty Pt transect). This model, however, while apparently falling-out an appropriate amount of copper in the northern harbour, does not produce the measured concentrations of copper in the southern harbour as does the conservative model results of which are given in the comparative profile plots of part 7 below (figs 5.28 to 5.38) along and south of the Sophia Pt–Liberty Pt transect.

There is hence a need to rationalise the two sets of results from the conservative and the adsorption/complexation model. Two arguments are as follows.

- The conservative model broadly represents the northern harbour in an average sense allowing an appropriate flux of copper across the Sophia Pt–Liberty Pt transect to obtain resulting levels of copper in the southern harbour which match the measured levels there.
- The adsorption/complexation model while matching in some detail with measured levels of copper in the northern harbour produces copper levels which are too low in the southern

harbour. This may indicate the need for a mechanism to be included which releases copper from the sediments, a distinct possibility given the favourable gradient for release of copper across the surface sediment/overlying water interface.

This rationalisation is important since measured copper concentrations in the southern harbour have been found to be toxic in the following sense. From earlier work (section 4) in which toxic copper concentrations were initially extracted from the MINTEQA2 modelling, it was found that where Cu⁺⁺ concentrations were present at toxic levels (3×10^{-9} M), those areas closely coincided with *total* copper concentrations of about an order of magnitude greater. Under this rule-of-thumb, from the field measurements of total copper, there are certainly toxic levels in the southern harbour. (A level of 3×10^{-8} M or $1.92 \mu g/L$ of total copper would constitute toxic levels as defined above.) This level is delineated by the second darkest blue contour band in the section plots of total copper which show such levels are not quite attained in the southern harbour with the adsorption/complexation model. They are, however, clearly attained there from the field measurements and from the conservative model (figs 5.28 to 5.38 of part 7 below.)

5.5 Section contour plots for toxicity northern harbour

These are plots of the free copper ion, Cu^{++} , as determined by MINTEQA2 equilibrium. They are a part of the adsorption/complexation model and are expected to be a reasonable representation of toxicity in the northern harbour as given by that model. A change of colour scale has been used to place emphasis on the range from nominally toxic conditions (3×10^{-9} M) to one order of magnitude above that threshold value. Again the second darkest blue contour band represents the beginning of toxic conditions and generally corresponds quite closely to the second darkest blue contour band in the plots for total copper in the northern harbour as discussed above.

5.6 Section plots for total copper conservative run

Having discussed the value of the conservative run in parts 3 and 4 above, it is illustrative to present section plots of the conservative run results covering almost the whole harbour. This is a series of four plots from the 10^{th} January to the 11^{th} March 1995 at 20-day intervals. The plots show the copper concentrations for this run reaching 'toxic' levels over most of the harbour and to a depth of at least 8 m. Compared with the analagous adsorption/complexation run results (figs 5.8, 5.10, 5.12 and 5.14) these concentrations can be considered to be high in the northern harbour (by a factor of about 2 overall) but quite representative of total copper concentrations in the southern harbour.

A strategy to merge these two model formulations (exhibiting behaviour to match field results over two different sections of the harbour) might be to lower the particle fall velocity to keep some of the copper, currently falling out, in the water column longer. This was considered but a settling velocity at the low end of the scale (10^{-4} m/s) for salt flocculation of fine cohesive sediments) has already been chosen. It is considered more appropriate to understand the possible effect of sediments as sources or sinks prior to further lowering the settling velocity in the adsorption/complexation model.

5.7 Profile plots for conservative and baseline runs

These plots provide a good overall indication of the validity of the modelling in terms of producing the steep halocline over the harbour from which pH conditions are set and used in the chemical modelling.

In regard to the concentrations of total copper, the plots show the decrease in harbour copper concentrations with distance southward of the Sophia Pt–Liberty Pt transect and also the tendency for higher concentrations to be found on the north-eastern side of the harbour. They compare the performance of the adsorption/complexation model and the conservative model at low concentrations (approaching the toxic threshold levels) and provide a clear indication that the conservative model gives results much closer to the available field measurements than does the adsorption/complexation model in the southern harbour. (As raised in part 4 above, this may be fortuitous by bringing higher levels of copper than measured across the Sophia Pt–Liberty Pt transect. The more appropriate (universal) model may, however, be the adsorption/complexation model equipped with a mechanism for the release of copper from sediments in the southern harbour.)

5.8 Section plot of cumulative sedimentation in northern harbour

This plot gives the comparative total cumulative copper fall-out (g/m^2) for the untreated (measured) and two treated scenarios in the King River delta region for the $4\frac{1}{2}$ month test period.

Since adsorption with fall-out of colloidal sediments is dominant the plot is of considerable interest showing the decrease of copper to sediments for the treated cases to be consistent with the percentage reductions in loadings. This result reinforces the finding that most of the copper deposits out with the settling of the sediments which form the King River delta.

5.9 Conclusions

The modelling procedure has proved better than expectations held at the commencement of the study. This positive assessment is largely based on the time-series plots (figs 5.1 to 5.6) and the profile plots (figs 5.28 to 5.38) which constitute a comprehensive comparison of chemical processes modelled, untreated/treated scenarios and the DELM field measurements taken in Macquarie Harbour over the $4\frac{1}{2}$ month test period.

No doubt the study could benefit from refinements such as further calibration of the hydrodynamics from moored current meter data, refined grid modelling of the northern harbour, particularly around the King River delta to better resolve the deposition process and inclusion of uptake of copper from the sediments throughout the harbour.

Nonetheless the study has yielded some interesting results as follows.

King River plumes disperse quickly with the majority of the copper adsorbing to hydrous metal oxides which undergo colloidal flocculation and sedimentation and fall-out close to the mouth forming the delta region. (Residual water column copper being well-modelled by the adsorption, deposition, complexation process.)

Potentially toxic conditions (using 3×10^{-9} M as a reference concentration for free Cu²⁺) were reached throughout the southern harbour over the 4½ month test period and were well-modelled by by the conservative case.

Typical proposed treatment scenarios for acid mine drainage will achieve the expected beneficial results (commensurate with the level of treatment) on the water quality in Macquarie Harbour with much less copper depositing and transporting within the water column.

Results of plume migration tests read in conjunction with, in particular figure 5.3 (Station 6), indicate that the region around Yellow Bluff will reach potentially toxic concentrations under 'untreated' conditions for both south-westerly and north-easterly winds. In contrast, under the 'treated scenarios', the region would largely achieve concentrations below the potentially toxic

level (2 μ g/L total copper) for the full range of conditions represented by the 4½ month test period.

Proposed improvements to the modelling facility now in place would be a fine grid treatment of the King River mouth and delta region to better spatially resolve the adsorption/deposition process coupled with a mechanism for the uptake of copper into the water column from the sediments harbour-wide.

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Appendix