T McBride

supervising scientist report

121

MOUNT LYELL REMEDIATION

Estimation of water quality over time within the Queen and King Rivers

David A Klessa, Lois Koehnken & John F Johnston

Mount Lyell Remediation
Research and Demonstration Program
a Tasmanian and Commonwealth Government initiative

supervising
scientist
report **121**

MOUNT LYELL REMEDIATION

Estimation of water quality over time within the Queen and King Rivers

David A Klessa, Lois Koehnken
& John F Johnston

Department *of* Environment
and Land Management

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.

David A Klessa–Environmental Research Institute of the Supervising Scientist

Lois Koehnken & John F Johnston–Department of Environment and Land Management

---

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

ISSN 1325-1554

ISBN 0 642 24321 2

Printed in Tasmania by Australian Government Printing Services.

Executive summary

A combined chemical-speciation and hydrological model has been developed to predict down stream changes in water chemistry in the Queen and King Rivers in response to possible remediative measures developed as part of the Mount Lyell Remediation Research and Demonstration Program (MLRRDP). A century of mining at the Mount Lyell copper mine in Queenstown, Tasmania, has resulted in massive volumes of tailings, smelter slag and acid drainage entering the Queen River, a tributary of the King River, and ultimately Macquarie Harbour. Acid drainage continues to enter the river system from the pumping of water from the active underground mine workings, and the draining of water from inactive mine workings and waste rock dumps. The aim of the MLRRDP, a cooperative program involving the Tasmanian and Commonwealth governments, is to develop remediation plans for the lease site, rivers and harbour which, if implemented, will begin to reverse the environmental impacts of historic mining practices, and promote the recovery of aquatic ecosystems.

The combined chemical-speciation and hydrological model was developed in order to fulfil the following objectives: predict changes in Queen and King River water chemistry in response to further development of the Mount Lyell mine or remediative measures to counter pollution from the Mount Lyell mine lease site; provide information which will assist in the development of a strategy for the biological recovery of the King and Queen Rivers based upon remediative measures at the mine lease site; supply boundary values and concentrations for pH and metals in the King River to permit the development of scenarios for the hydrodynamic modelling of Macquarie Harbour; and, to compare biological response under test conditions with speciation predictions to help elucidate the principal factors determining ecotoxicological reaction.

The model consists of two parts: the first deals with dilution of mine effluent by unimpacted river water and the second with speciation predictions based upon the composition of the mix and its chemical equilibria using MINTEQ2A (ver 3.11). The mixing model was based on a single source of acid drainage and two unimpacted diluents, namely the Queen and King River. Unimpacted waters in both these rivers typically have a very low suspended solids content and alkalinity. The composition of acid drainage was taken as the median concentration of constituents from a combined Conveyor Tunnel and North Lyell Tunnel source representing about 78% of the Cu load from the Mount Lyell lease. The diluents were also based on median concentrations, albeit from a very limited data set. Mixing of acid drainage with river water was modelled using either a geometric dilution series for the Queen River and King River with the power station off, or in the case of the power station on, Lake Burbury providing 80 cumecs and median flow from other sources.

Because results from MLRRDP investigations indicate that the major effort in countering the impact of acid drainage will have to be liming so long as mine effluent has direct passage to local creeks and rivers, the scenarios which were modelled were equivalent to the proportion of total acid drainage which might be neutralised under different remediation strategies. The four most likely remediation scenarios which were modelled were: 8% neutralisation of acid drainage (current situation); 65% neutralisation of acid drainage corresponding to the neutralisation of Conveyor Tunnel discharges; 80% neutralisation of acid drainage corresponding to the treatment of the North Lyell Tunnel discharges in addition to the Conveyor Tunnel; and 99% neutralisation of acid drainage sources which also includes the discharges from the West Lyell waste rock dumps. Neutralisation endpoints of pH 6.5 and pH 5.5 were modelled for each of the above described scenarios, as was the inclusion/exclusion of a copper-recovering Solvent Extraction/Electrowinning (SX/EW) plant prior to neutralisation.

In the model, the neutralised acid drainage was re-mixed with the remaining acid drainage sources and 'released' downstream. It was assumed that the precipitation products formed from the neutralisation reaction were not discharged into the Queen River. A conservative approach was taken for the downstream speciation modelling in that the sorption of metals by either naturally occurring suspended matter or precipitates, which were predicted to form from components of the acid drainage, was not invoked. The concentration of natural suspended solids in Lake Burbury water, the principal source of the King River, is exceedingly low (typically 1–2 ntu), and are therefore unlikely to influence solution phase chemistry to any marked degree.

The model results have extremely important implications for the development of remediation strategies and the recovery of the Queen and King Rivers. One of the most important findings is that there is little scope for recovery of the King River based on the predicted bioavailability and toxicity of copper unless almost *all (>99%)* of the acid drainage currently entering Haulage Creek is neutralised to pH 6.5. Additionally, the use of SX/EW technology in conjunction with neutralisation of acid drainage to pH 5.5 confers less advantage in terms of potential copper toxicity to aquatic life compared to neutralisation to pH 6.5. Hence, if SX/EW is to proceed, no advantage will be realised by the downstream ecosystem unless all raffinate is neutralised to pH 6.5. The model results also indicate that even if this very high target of 99% treatment of acid drainage can be achieved, the ecological recovery of the Queen River may continue to be hampered due to toxicological impacts associated with copper.

Aluminium, another metal of concern for the recovery of the river system, was more difficult to evaluate due to a high degree of uncertainty about the relative toxicities of Al species to aquatic organisms, and because of the paucity of available data pertaining to background concentrations in the King River catchment. However, model results suggest that aluminium concentrations may be reduced to tolerable concentrations if somewhere between 80% and 99% of the acid drainage is neutralised to a pH of 5.5, conditions under which copper would continue to remain the limiting factor.

The toxicological impacts of fluoride, manganese and iron were also examined with the conclusion that fluoride is present in sufficiently high concentration in acid drainage to pose constraints to biological recovery and liming to pH 6.5 is required to promote the precipitation of fluorite during neutralisation. Manganese and iron were found to probably be far less of a constraint to biological recovery in the Queen and King Rivers than either copper or aluminium.

The speciation predictions from the model could be refined through the collection of additional geochemical input data, especially with respect to background concentrations of metals in the King River catchment, and DOC concentrations.

Validation of model predictions was outside the scope of this project. Clearly, however, there is a need to test the predictions provided under the modelled scenarios by laboratory-based mixing experiments and, if necessary, to adjust the model to take account of kinetics and chemical processes such sorption and precipitation. In particular, the importance of a suspended Fe oxy-hydroxide phase in river water derived from the mixing of acid and neutralised drainage with river water requires to be elucidated with respect to its role to adsorb, and possibly coprecipitate Cu.

Contents

Figures

Tables

Acknowledgments

We are grateful to the following for their assistance:

Copper Mines of Australia, particularly Alan Robertson and Isobel Stanley, for the provision of data and advice.

Climate and Consultancy Section, Tasmania and Antartica Regional Office of the Bureau of Meteorology for Mount Lyell historical rainfall data.

Hydro-Electric Commission, Tasmania, for Conveyor Tunnel flow rate data.

Andrew Sanger, Inland Fisheries Commission, Tasmania, for information on the natural suspended solids content of waters in SW Tasmania.

Chris leGras and Arthur Johnston for useful comments on the script and to the former for considering the kinetics of fluoro-aluminium complexation.

Karen Johnston as the organiser of data and messages between Queenstown and Jabiru.

Joan Mount for providing interlibrary loans speedily and at short notice.

1 Introduction

A century of mining in the Mount Lyell region has impacted upon the economics, social history and natural environment of the locale (McQuade et al 1995). Marked changes have occurred to the physiography, hydrology, biogeochemistry and ecology of the local terrestrial and riverine systems and affected marine receiving waters in Macquarie Harbour. However, until recently, mining impacts, particularly to the aquatic environments, had neither been well described nor quantified.

The establishment of the Mount Lyell Remediation Research and Demonstration Program (MLRRDP) in 1995 by the Tasmanian Department of Environment and Land Management's Division of Environment and Planning (DEP), the Environmental Research Institute of the Supervising Scientist (***eriss***) and the Office of the Supervising Scientist (***oss***) has sought, under the auspices of the Tasmanian and Federal Governments, to delineate the environmental impacts arising from mining and develop a strategy of remediation and environmental rehabilitation. The project contained in this report forms part of the MLRRDP and deals with changes in water quality in the Queen and King Rivers resulting from mining at the Mount Lyell lease site based upon mining and water management practices now and into the future.

A history of mining in the Mount Lyell region is documented elsewhere (McQuade et al 1995) and will only be described briefly here in the context of impact on the river systems. From 1915 until December 1994, an estimated 97.4 million tonnes of tailings were disposed into Haulage Creek (Locher 1995) by the former Mount Lyell Mining and Railway Company Limited (MLMRCL) and thence transported by the Queen and King Rivers into Macquarie Harbour. In addition, around 1.4 million tonnes of slag was co-disposed with tailings between 1929–1970 (Locher 1995) and over the whole time frame the sediment load was augmented by the accelerated erosion of topsoil from the lease site (MLMRCL 1990). Locher (1995) has studied the distribution of sediment within the King River resulting from mining and ascribed about 3.4 and ≤10 cubic metres respectively to deposition in sediment banks and the river bed. In addition, Koehnken (1996) has estimated the King River delta to contain 100 million cubic metres of sediment.

The mining of the pyritic host rocks of the Mount Lyell region has led to, and continues to provide, large inputs of acid drainage to the Queen and King Rivers from mine dewatering, old workings and waste rock (McQuade et al 1995, Miedecke 1996) with acid generation from the latter predicted to continue in the absence of remediation for 600 years (Garvie & Gibson 1994). As well as acting as a major source of acidity, the mine drainage supplies a significant flux of metals (copper, aluminium, iron and manganese) and sulphate to the Queen catchment. In this regard, Miedecke (1996) estimates a daily flux of 2.5 tonnes of copper entering the Queen River representing 99.3% of its load and 98.7% of copper export from the lease site in drainage waters. Importantly, the discharge of limed tailings at the moderately alkaline pH 9.5 by the MLMRCL into the Queen River mitigated the effects of acid drainage on the soluble concentrations of metals by pH buffering and, in the presence of oxy-hydroxide precipitates, by providing a large surface for metal sorption.

The cessation of tailings disposal and closure of the Prince Lyell mine in December 1994 resulted in a marked decrease in pH and large increases in dissolved metal concentrations in the King River (Koehnken 1996). For example, prior to mine closure, dissolved copper concentrations were typically 200–300 µg/L rising in excess of 30-fold once tailings disposal ended and gave rise to copper rich plumes (>1000 µg/L) within Macquarie Harbour (Koehnken 1996).

In late 1994, Copper Mines of Tasmania (CMT) took over operation of the Mount Lyell mine under an Agreement between the Tasmanian Government and the Company. The Agreement is described formally by the *Copper Mines of Tasmania (Agreement) Act 1994* by which the Company became committed to building a tailings dam to hold all solid effluents from their operations (CMT 1995) equivalent to an annual ore processing rate of 3.5 million tonnes over 60 years (McQuade et al 1995). In addition, CMT indicated their intention to use the neutralisation capacity of tailings to treat a portion of the acid drainage thereby reducing the flux of acidity and contaminants into the Queen River (CMT 1995). Currently, CMT are treating 20% of Conveyor Tunnel water to between pH 6.5–7.5 (J Johnson, pers comm). Miedecke (1996) has reviewed options for remediating acid drainage from Mount Lyell including the establishment of a solvent extraction/electrowinning (SX/EW) plant to remove copper. This would entail the neutralisation of raffinate prior to disposal to the Queen River and has been suggested as providing a viable, economic long-term strategy in accordance with the principle of best practicable technology to counter the export of acidity and metals to the Queen and King Rivers. Other remediative measures dealing with local sources of acid drainage have also been canvassed (Miedecke 1996).

The basis of the project contained in this report follows on from a study conducted on behalf of MLMRCL by Environmental Geochemistry International (EGI) Pty Ltd. (MLMRCL 1995a) in which speciation modelling was used to predict changes in river water chemistry resulting from mine closure. EGI termed this model *Rivchem*. A similar approach has been adopted here but with the emphasis placed on predicting the effects on river water chemistry of remediative actions concurrent with active mining by using a flexible, generic model whose outcomes are insensitive to the detail of decisions concerning remediation, ore processing and water management. Results from this study have also been used to help establish boundary conditions for a hydrodynamic model of Macquarie Harbour and to assist in relating ecotoxicological response to chemical speciation predictions as part of the MLRRDP. Consequently, this project has the following objectives:

- to develop a speciation model having general application, based on the *Rivchem* approach, which predicts changes in Queen and King River water chemistry in response to:
    - further development of the Mount Lyell mine;
    - remediative measures to counter pollution from the Mount Lyell mine lease site;
- to provide information which will assist in the development of a strategy for the biological recovery of the King and Queen Rivers based upon remediative measures at the mine lease site;
- to supply boundary values and concentrations for pH and metals in the King River to permit the development of scenarios for the hydrodynamic modelling of Macquarie Harbour;
- to compare biological response under test conditions with speciation predictions to help elucidate the principal factors determining ecotoxicological reaction.

2 Chemistry of the Queen and King River catchments

2.1 Background

The natural river waters of south-west Tasmania are typified as soft having a low conductivity, alkalinity and suspended solids content; moderately acid pH; and moderately-high dissolved organic carbon (Buckney & Tyler 1976; Koehnken 1996). With the exception of the East Queen River and Haulage Creek (which hosts effluent from Mount Lyell mine and has its confluence with the Queen River approximately 200 m below the lease site (table 2.1)), all other subcatchments of the Queen River and have remained unimpacted from major mining (fig 2.1). However, the decision to place the tailings dam in the Princess catchment has meant that, henceforth, dam decant will cause a deterioration in water quality of the Princess Creek (CMT 1996) particularly from elevated pH and conductivity arising principally from increased sulphate, calcium, magnesium and manganese (table 2.2).

Table 2.1 The subcatchments of the Queen and King Rivers (after Locher 1995). Impacted areas from mining at Mount Lyell are shown in italics.

Queen River		King River (below Queen River confluence)	
Catchment name	**Area (ha)**	**Catchment name**	**Area (ha)**
West Queen	800	Newall	900
East Queen	*550*	Un-named	630
Haulage	*287*[1]	Garfield	4800
Conglomerate	500	Sailor Jack	630
Roaring Meg	300	Open	650
Un-named	200	Fleabite	300
Lynch	500	Un-named	120
Princess	*1300*	Swift	2500
Un-named	250	Lower Landing	140
Halls	650	Virginia	700
		Four-Mile	200
		Cutten	150
		Kingfisher	220
		Lucky	100

[1] From McQuade et al (1995)

While water quality in the Lower King River has been and continues to be severely impacted by flow from the Queen River, Lake Burbury in the Upper King catchment, which receives flow from the Comstock and Linda subcatchments, remains relatively unaffected by mining at Mount Lyell. In recent years, remediative works have been conducted to reduce acid and metal fluxes into Lake Burbury (McQuade et al 1995). Best estimates indicate that around 1% of daily copper flux from Mount Lyell enters Lake Burbury but currently this appears to have had little effect on water quality probably because of the combination of attenuation by sorption and dilution in the lake.

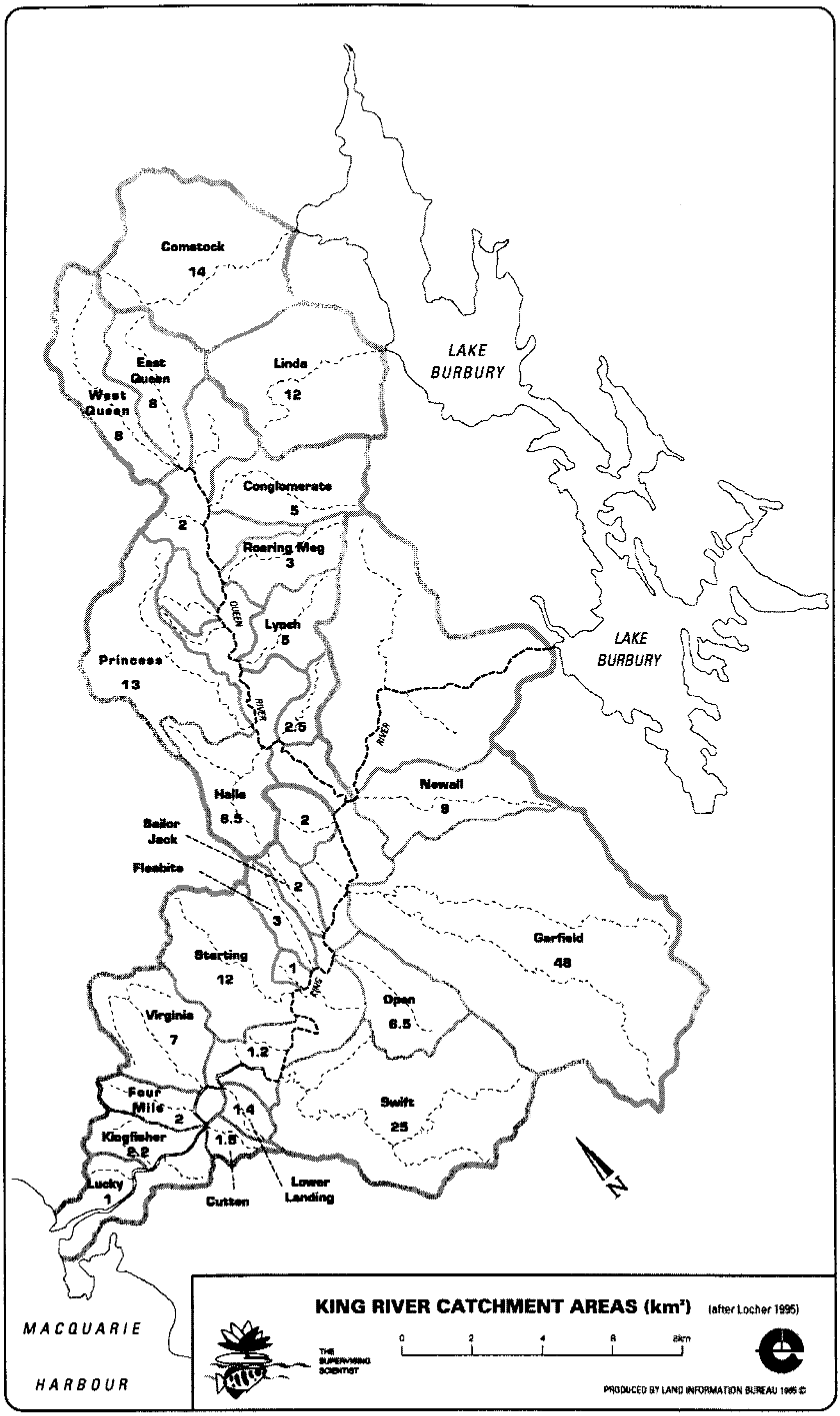


Figure 2.1 Regional surface water drainage network of the Mount Lyell mine and vicinity

Table 2.2 Ambient water quality of dissolved constituents in Princess Creek and predicted composition of decant from the tailings dam (CMT 1996)

Parameter (all units mg/L except pH)	Princess Creek	Dam decant
pH	4.4–7.2	6.0–7.3
Total suspended solids	<44	NR
Dissolved organic C	9	*10?*
Ca	2	*20?*
Mg	NR	10
SO_4	6–*144*	500
F	NR	1
Fe	0.24–0.60	0.24–0.60
Al	0.8–*29*	0.8–*29*
Mn	<0.3	5–10
Cu	0.007–0.040	0.02
Zn	<0.01	0.1
Pb	<0.008	<0.001

Note: Data placed in *italics* is suspect

2.2 The composition of unimpacted (diluent) river water

There is a paucity of data on the composition of unimpacted river water in the Queen and King catchments. This is surprising given the use that has been, and is being made, of clean river water from the West Queen for mill water supply at Mount Lyell. It is also of concern on two counts. First, there is a clear need for a sound water quality database for the region upon which to judge the extent to which remediation results in the improvement of water quality to some set of baseline values. Second, the value of the predictions of a model are obviously limited by the quality of the input data. Hence, the absence of good baseline data potentially places some difficulties on the interpretation of model outcomes especially where quantification of impact is required.

To our knowledge, available data are restricted to two small datasets for the West Queen and Princess Creek which are summarised in table 2.3. Carpenter et al (1991) also provide some background information on the composition of the Upper King River. Table 2.3 demonstrates the deficiencies in the available data and highlights the need to verify the composition of unimpacted waters of the King and Queen catchments. While the Princess Creek data precedes the first decantation of tailings dam water on 25 May 1996 (I Stanley, pers comm), local disturbance by machinery movement and building works probably enhanced solute loads and this leads to some doubt about the veracity of key chemical indicators, particularly total suspended solids (TSS), sulphate, aluminium, copper, manganese and possibly iron. In addition, comparison of the West Queen and Princess Creek catchments with the Upper King indicates that dissolved metals are at least one to three orders of magnitude less in the latter which raises the question as to whether these are true differences which can be attributed to mineralisation in the West Queen (ie geological and geochemical contrasts between the areas) or whether they have arisen from differences in sampling and analytical techniques.

In the absence of verifiable data to represent the composition of unimpacted waters and for the sake of consistency in approach, the median concentrations derived by EGI (MLMRCL 1995a) for their *Rivchem* model, with the exception of Fe and Al, were used as default values for Queen River subcatchment waters (table 2.4). There is some evidence to suggest that the pH of the Upper King River (Carpenter et al 1991) and Lake Burbury (L Koehnken, pers comm) is higher than in the Queen catchment. Hence for modelling dilution in the Lower

King River, a pH of 6.2 for Lake Burbury was assumed. In the absence of field data, the remaining suite of chemical constituents was taken to be the same as for the Queen (table 2.4). It should be noted, however, that the total dissolved concentrations adopted by *Rivchem* for Fe (0.5 mg/L) and Al (0.4 mg/L) are abnormally high if ferrihydrite and gibbsite are assumed to be the principal mineral phases determining respective solubilities either at pH 5.5 or 6.2. Under natural conditions, however, concentrations of soluble (ie <0.45 µm) Fe and Al may appear to exceed the solubilities of controlling mineral phases because of the presence of colloidal forms. This is further discussed in section 6.

Table 2.3 Mean (± SD) and median dissolved (mg/L) constituents in river water of the Queen and King catchments

	West Queen	**Princess Creek**		**Upper King**
Sampling point	MLMRCL #12	Lower (Lynchford)	Upper (below dam)	Unknown
Source of data	MLMRCL	CMT	CMT	Carpenter et al (1991)
Time of sampling	April 74–March 75	April 95–May 96	May 95–May 96	1989?
Mean pH	5.35 ± 0.64; n = 13	6.06 ± 0.81; n = 26	5.32 ± 0.80; n = 52	6.9
Median pH	5.50	6.2	5.3	–
Mean DOC	–	10.3 ± 4.9; n = 16	10.9 ± 6.5; n = 16	–
Median DOC	–	9.6	8.8	–
Mean TSS	9.2 ± 6.0; n = 12	21.1 ± 33.2; n = 26	44.4 ± 87.9; n = 52	–
Median TSS	10	7.5	13.5	–
Mean Na	–	7.7 ± 0.6; n = 14	6.8 ± 2.1; n = 14	–
Median	–	7.6	7.5	–
Mean K	–	0.9 ± 0.3; n = 14	1.2 ± 0.7; n = 14	–
Median K	–	0.8	1.0	–
Mean Ca	–	5.6 ± 1.9; n = 6	2.5 ± 1.5; n = 38	–
Median Ca	–	4.8	2.2	–
Mean Mg	–	1.8 ± 0.3; n = 6	–	–
Median Mg	–	1.8	–	–
Mean Cl	–	12.9 ± 1.7; n = 14	11.9 ± 1.7; n = 14	–
Median Cl	–	12.5	12.0	–
Mean SO_4	–	16.8 ± 35.7; n = 26	14.2 ± 16.0; n = 52	–
Median SO_4	–	8.8	10	–
Mean Cu	–	0.021 ± 0.015; n = 26	0.064 ± 0.067; n = 14	0.0008
Median Cu	–	0.018	0.029	–
Mean Zn	0.107 ± 0.053; n = 17	0.024 ± 0.016; n = 12	–	<0.00001
Median Zn	0.100		–	–
Mean Fe	–	0.309 ± 0.104; n = 12	–	0.089
Median Fe	–	0.295	–	–
Mean Al	–	2.697 ± 8.285; n = 12	–	–
Median Al	–	0.25	–	–
Mean Mn	0.106 ± 0.024; n = 17	0.032 ± 0.025; n = 12	–	0.0066
Median Mn	0.100	0.025	–	–

Note: DOC is dissolved organic carbon and TSS is total suspended solids.

Table 2.4 Dissolved (mg/L) constituents in unimpacted Queen and King River and Lake Burbury water used in the model

Source	pH	Ca	Mg	Na	K	Cl	SO_4	Fe	Mn	Al	Cu	DOC
Queen/King	5.5	1	1	4	0.5	12	3	0.030	0.01	0.075	0.005	10
L Burbury	6.2	1	1	4	0.5	12	3	0.006	0.01	0.019	0.005	10

2.3 The composition of impacted river water

Background information on the composition and speciation of the Queen and King River waters during MLMRCL's operation of Mount Lyell mine is contained elsewhere (MLMRCL 1995a,b,c) and predicts the implications to water quality of an end to tailings disposal into the Queen River. The closure of the mine in December 1994 and the subsequent effects of acid drainage on the water quality of the King River and Macquarie Harbour based on field observations are discussed by Koehnken (1996) and will not be treated further here.

2.3.1 Acid mine drainage

The discharge of acid drainage from the Mount Lyell lease into the Queen and King Rivers has repercussions to the health of these systems mainly for two reasons. First, the acid drainage is a source of potential ecotoxicity by virtue of its high ionic strength and concentrations of Cu, Fe, Mn, Al and F. Second, the natural water of the catchments has low alkalinity and this in conjunction with the high total acidity of the effluent gives rise to low pH even at relatively high dilutions by river water.

The composition of acid drainage at Mount Lyell is dependent upon its derivation and is subject to temporal variation in response to antecedent conditions, particularly rainfall quantity and pattern. A summary of median pH, sulphate and total soluble metal concentrations from a number of sampling stations on the Haulage Creek catchment is given by McQuade et al (1995) based largely on monthly data and is summarised in table 2.5. However, the variability in the composition of acid drainage between sites and the relative importance of each as a pollution source is better expressed in the form of flux as given in table 2.6.

Table 2.5 Median composition (mg/L) of soluble components of acid drainage from sources in the Haulage Creek catchment and median flow rates*

Source	Cu	Fe	Zn	Mn	SO_4	pH	Flow rate (L/s)
West Lyell waste rock dumps	82	777	5.9	46	6430	2.4	54
West Lyell Tunnel	14	223	4.7	38	2100	2.9	4
North Lyell Tunnel	54	319	4.6	21	1655	2.8	56
Conveyor Tunnel	134	246	16.6	167	3995	2.8	92
Magazine Creek (by difference)	22	599	–	412	4133	–	19
Haulage Creek	90	421	9.3	120	3975	2.7	225

* From McQuade et al (1995)

High acidities arise from the oxidation of sulphides either in gangue or the country rock to produce sulphuric acid which, following the hydrolysis and solution of host minerals, results in elevated concentrations of Fe, Al and Mn. The role of these metals in buffering acidity is discussed in section 2.3.2. While the greatest source of acidity on the Mount Lyell lease site comes from the West Lyell waste rock dumps (table 2.6), the highest copper concentration and flux derives from underground workings where water is in contact with mineralised zones.

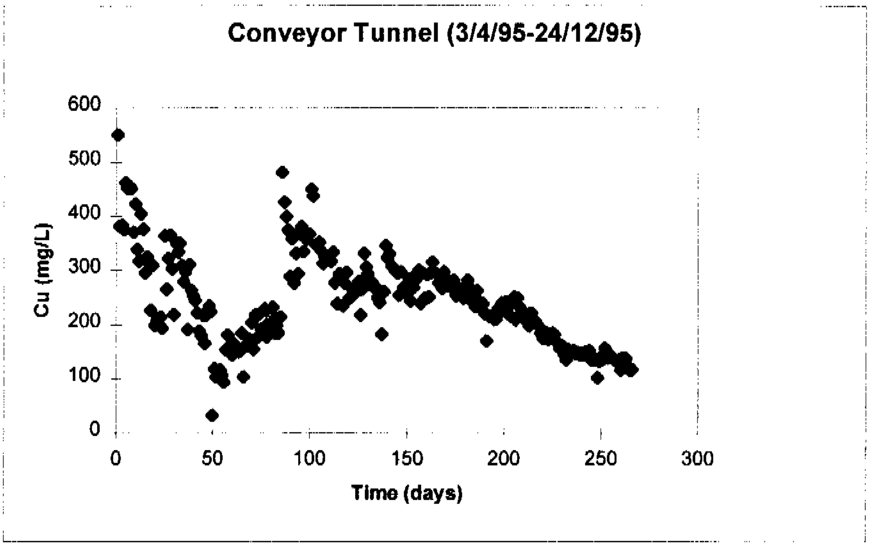


Figure 2.2 Copper concentration (mg/L) in Conveyor Tunnel discharge during 1995

Table 2.6 The relative contribution of sources of acid drainage to total soluble copper and acidity fluxes from Mount Lyell

	Contribution (%)	
Source	**Copper**	**Acidity**
West Lyell waste rock dumps	21.0	39.8
West Lyell Tunnel	0.2	1.1
North Lyell Tunnel	14.0	11.7
Conveyor Tunnel	64.0	33.5
Magazine Creek	0.8	13.9

Note: after Miedecke et al (1996) and L Koehnken & J Johnston (pers comm)

With the exception of data for Conveyor Tunnel recently gathered by CMT (fig 2.2), there is little information upon which to gauge daily variation in the composition of acid drainage. During 1995, Cu was commonly above 200 mg/L in Conveyor Tunnel discharge and showed two maxima of around 500 mg/L at the start of the sampling period in early April and in late June/early July, well above the median concentration of 134 mg Cu/L (table 2.4). It is probable that the first peak represents the residual effects of an extremely dry period that coincided with the closure of MLMRCL operations at the end of 1994 and which encouraged the *in situ* oxidation of sulphidic minerals. Rainfall records for Mount Lyell (Bureau of Meteorology 1996) indicate that December 1994 (52.8 mm), January 1995 (92.4 mm) and February 1995 (90.6 mm) belong to decile 1, 3 and 4 respectively, where decile 1 represents the rainfall amount in the category having the lowest (ie 0–10%) frequency of occurrence for the stated month. If rainfall over a three month time frame (ie December 1994–February 1995) is related to frequency of occurrence, then it too is found to belong to the decile 1 range (ie 158–296 mm). The second peak in late June/early July happened at the resumption of underground mining by CMT. By the end of the year, Cu concentrations had fallen to around the median value of 140 mg/L and weekly records since then (ie to March 1996) have indicated that Cu levels have averaged 160 mg/L (John Johnston, pers comm). This pattern in concentration variation by Cu (fig 2.2) has also been shown by the associated metals and non-metals in acid drainage including Fe, Al, Zn, Mn, SO_4 and F. Estimated Cu load from Conveyor Tunnel for the nine month period April–November 1995 was 1.74 t/day, well above the annual estimate (L Koehnken & J Johnston, pers comm) of 1.20 t based on median data (McQuade et al 1995).

Since April 1995, Conveyor Tunnel discharge has been rerouted into North Lyell Tunnel. For the purposes of modelling, the composition of acid drainage (table 2.7) was typified by taking account of median flow rates (table 2.5) and combining the median concentrations of Conveyor and North Lyell Tunnel waters which collectively contribute 78% and 45% of Cu and acidity fluxes respectively in Haulage Creek (table 2.6). Where data on median concentrations for specific constituents were absent, values quoted either by EGI or CMT were used.

Table 2.7 Median composition (mg/L) of soluble constituents in Conveyor Tunnel, North Lyell Tunnel and combined acid drainage

	Source		
Constituent	**Conveyor Tunnel**	**North Lyell Tunnel**	**Combined**
pH	2.8	2.8	2.8
Ca	150	50	112
Mg	450	150	336
Na	6	6	6
K	2	2	2
Cl	12	12	12
F	25	25	25
SO_4	3995	1655	3110
Fe	246	319	274
Mn	167	21	112
Al	210	70	157
Cu	134	21	104
Zn	17	5	12

Note: Data for pH, Fe, Al, Mn, Zn and SO_4 from McQuade et al (1995); Ca, Mg, K, Na and Cl from MLMRCL (1995a); F from CMT records (J Johnston, pers comm)

2.3.2 Neutralisation of acid drainage

Amongst the options which have been canvassed to reduce the impact of acid drainage on the river systems has been its (partial) neutralisation by liming material (Miedecke 1996). Currently, CMT is treating around 20% of Conveyor Tunnel drainage by bringing it into contact with limed tailings to achieve pH 6.5.

Depending on the target pH, liming can be a very effective means of reducing metal concentrations and loadings in mine waters. The titration curve of acid drainage is typically polybasic in form (fig 2.3) reflecting the phased precipitation of Fe, Al and Cu in that order to an endpoint of pH 6.5. In a laboratory experiment, increments of calcium hydroxide were added to 50 ml acid drainage from Conveyor Tunnel. Concentrations of total soluble metals in the treated acid drainage after neutralisation to pH 6.5 were as follows (mg/L); Cu 0.09, Fe 0.08, Mn 55 and Al <0.1. While there is good agreement between measured and theoretical lime requirements at pH 6.5, and in the form of the buffer curve at its extremes, the model did not provide a good fit in the pH range 3.1–4.8. This could either be attributed to the conditions under which the speciation model was used (which are discussed in section 4) and/or to the assumption that equilibria had been attained in the laboratory experiment. A downward pH drift to 6.2 after 24 h indicated that true equilibria had probably not been attained between the precipitate and solution phases.

Previous work (MLMRCL 1995c) examined the buffering characteristics of Haulage Creek water using 0.1 M NaOH and found a lime requirement to pH 6.5 of 0.023 mol/L. In addition changes in Cu, Fe and Al were documented as a function of pH. However, these results have to be treated with caution since the products of reaction using NaOH as opposed to a liming material will be different by virtue of their effects on the solution phase and its stoichiometry. For example, the use of lime, in the presence of high sulphate concentrations, will force the precipitation of gypsum and thereby affect other potential reactions involving Al and Cu which can form hydroxy-sulphate salts. Hence, differences in the products of reaction between NaOH and lime will influence pH buffering, composition of the solution phase and the derivation of lime requirements.

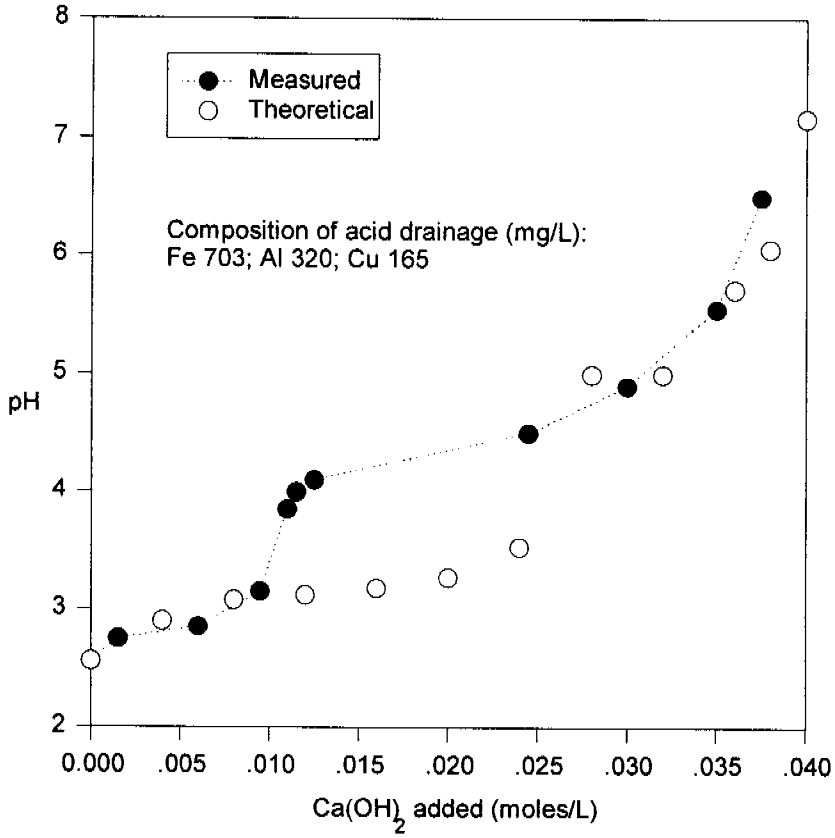


Figure 2.3 Measured and theoretical buffer curves for Conveyor Tunnel acid drainage

2.3.3 Other sources of potential contaminants

Apart from the discharge of acid drainage to the Queen River from the Mount Lyell mine, the other principal sources of mine-derived contaminants in the Queen and King River catchments are tailing levees and river bed slag. A description of their distributions, modes of occurrence and mineralogies are contained elsewhere (Locher 1995, Taylor et al 1996). It has been estimated by Taylor et al (1996) that about 2.9 kg Cu/day enters the King River from the tailings banks via groundwater seepage and that this is probably matched by a flux of similar magnitude from surface water flow. If this is correct, Cu loads of the order of 6 kg/day would represent less than 0.3% of the Cu in acid drainage flux at Mount Lyell and would give rise to an average +0.01 mg Cu/L in the King River assuming median flow conditions with power station off (see section 4) and constant rate of Cu flux from the tailings. The contribution of river bed slag to Cu concentration in the King River has not been evaluated.

3 Hydrological modelling of the Queen and King River catchments

3.1 Introduction

In this section, data that were used to develop a simple dilution model for acid drainage input into the Queen and King Rivers are summarised based upon median flow rates of the subcatchments of each river system (fig 2.1). In addition, attention has been given to the variability in flow of Conveyor Tunnel because plans to counter high Cu and/or acidity in underground mine waters prior to release are dependent on a treatment processing rate which is likely to require storage time for acid drainage under high flow conditions. Further background on the hydrology of the Queen and King catchments is given by Locher (1995).

3.2 Queen and King River subcatchments

The areas and median flows of the subcatchments of the Queen River are listed in table 3.1 together with the dilution rate of acid mine drainage downstream of Haulage Creek entry assuming that the John Butters Power Station is not operating. In the absence of data, the areal extent of mixing zones for waters have remained undefined. Areas of subcatchments are taken from Locher (1995) and are shown in fig 2.1, although these are considered as very rough estimates only (H Locher, pers comm). Median flow rates were calculated using an equation derived by HEC (1988) for individual small subcatchments of the King and Queen Rivers as given by Locher (1995) and EGI (MLMRCL 1995a) as follows:

$$F = (19.3+5.4*\log A)*A$$

where F = flow rate (L/s); A = area of subcatchment (km^2)

Median flow rates for the catchments of the Queen and King Rivers are estimated to be 1436 and 3887 L/s respectively with a median flow rate of King River water entry to Macquarie Harbour of 5323 L/s. It should be noted that while there is generally good agreement between the estimates of catchment flows by Locher (1995) and EGI (MLMRCL 1995a) for the Queen River system, EGI estimated the median flow contribution of the King River catchment alone to be 5195 L/s with the addition of Queen River water providing a total flow of around 6500 L/s into Macquarie Harbour. However, EGI are likely to have overestimated the King River median flow downstream of the Queen River confluence because it was calculated on the assumption of a single subcatchment having an area of 131 km^2 thus representing both a misuse of the HEC equation and, possibly, an exaggerated total area of the total King River catchment. If the EGI data is taken as correct, then dilution of acid drainage in the King River would approximate to 3%.

3.3 Conveyor Tunnel flow

A study of flow in Conveyor Tunnel is deemed important for two reasons. First, information on the likely variability in the flow rate of acid drainage into Haulage Creek assists in setting expected boundary maximum and minimum concentrations of potential contaminants in receiving waters. Second, it has been proposed as an option that Cu might be recovered economically from mine waters using technology offered by solvent extraction (SX) in conjunction with electrowinning (EW) (Miedecke 1996). It is likely that an SX/EW plant if built would process a maximum rate of 100 L/s of acid drainage (W Jones, pers comm) so flow in excess of this figure would require a holding facility if all acid drainage in Conveyor Tunnel was to be processed or, alternatively, untreated excess would enter the Queen River.

Two sets of data were obtained courtesy of HEC. The first analysed by HEC and summarised in fig 3.1, shows the distribution of flow in Conveyor Tunnel between 20/2/95–1/6/95 based on continuous recording.

Table 3.1 The area and median flow rate of subcatchments of the Queen and King Rivers and their effect on the dilution of acid drainage from Haulage Creek

Subcatchment	Area (km^2)	Median flow (L/s)	Dilution rate
Headwaters of East Queen	2.4	51.2	–
Upper East Queen (East Bank)	0.88	16.7	–
Upper East Queen (West Bank)	1.2	23.7	–
Lower East Queen (East Bank)	0.6	10.9	–
Lower East Queen (West Bank)	0.84	15.9	–
Cape Horne mine and waste rock area	0.68	12.5	–
Crown Lyell waste rock area	1.15	22.6	–
West Queen	7.6	183	
Queen River – Upstream of Haulage Creek	***15.35***	***336.5***	–
Haulage Creek	–	***225***	1:1.5 (41.1%)
Conglomerate Creek	5	115.4	1:2 (33.2%)
Lower Queen	32	759.6	1:5.4 (15.7%)
Queen River – Downstream of Haulage Creek	***52.35***	***1436.5***	–
King River subcatchment (d'stream of King R. Power Station)	25?	671.2?	1:8.4 (10.7%)
Newall	9	220.1	1:9.3 (9.7%)
King River confluence with Queen River	***86.35***	***2327.8***	–
Un-named	2	41.9	1:9.5 (9.5%)
Garfield	48	1362.2	1:15.6 (6.0%)
Sailor Jack	2	41.9	1:15.8 (6.0%)
Open	6.5	154.0	1:16.5 (5.7%)
Fleabite	3	65.6	1:16.7 (5.6%)
Starting	12	301.5	1:18.1 (5.2%)
Un-named	1.2	23.7	1:18.2 (5.2%)
Swift	25	671.2	1:21.2 (4.5%)
Lower Landing	1.4	28.1	1:21.3 (4.5%)
Virginia	7	167.0	1:22.0 (4.3%)
Four-Mile	2	41.9	1:22.2 (4.3%)
Cutten	1.5	30.4	1:22.4 (4.3%)
Kingfisher	2.2	46.5	1:22.6 (4.2%)
Lucky	1	19.3	1:22.7 (4.2%)
King River (above delta)	***201.1***	***5323***	

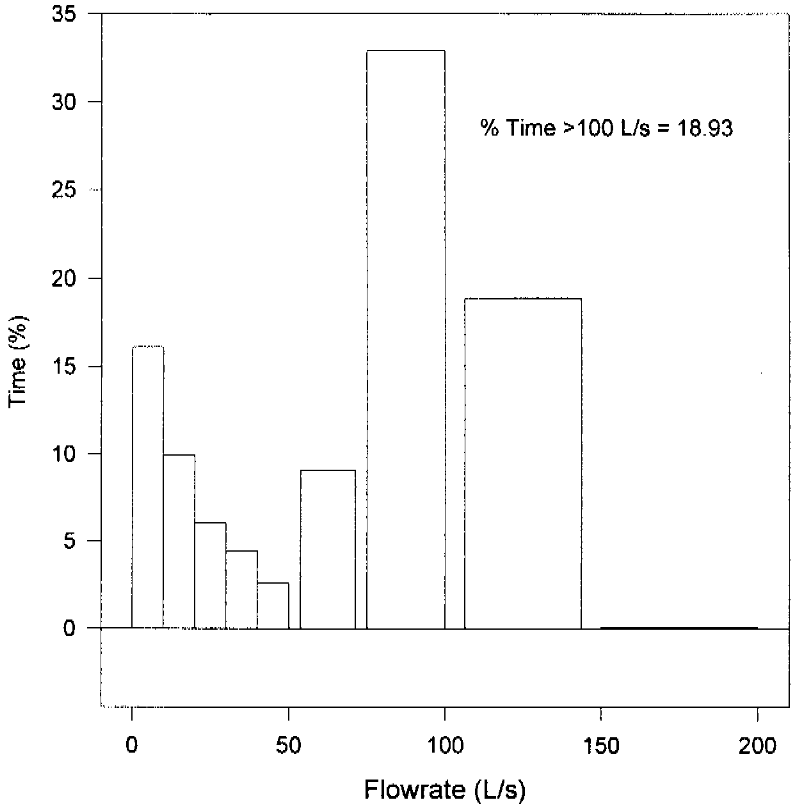


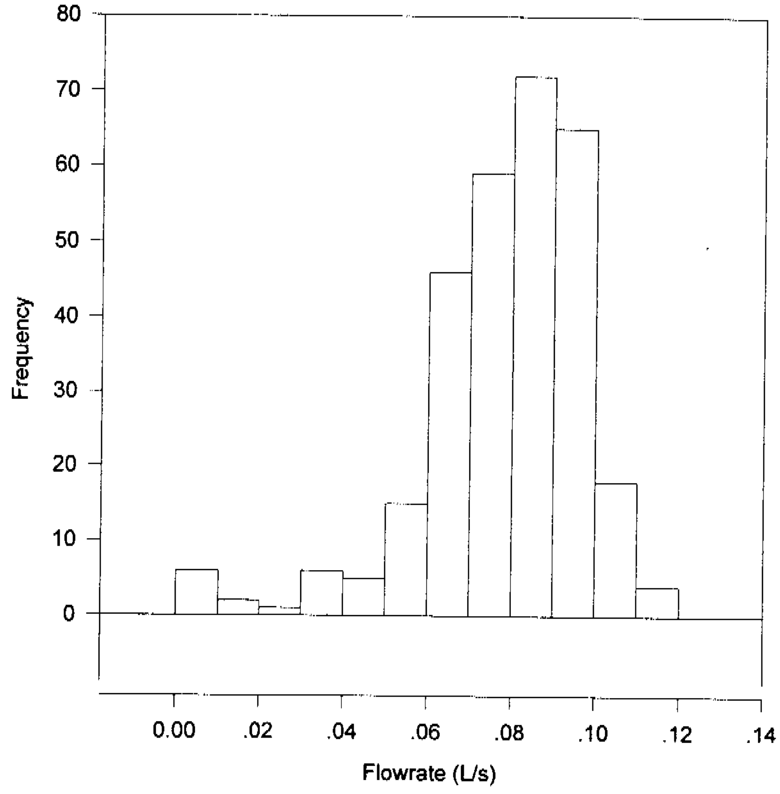
Figure 3.1 Frequency distribution of flow rates in Conveyor Tunnel 20/2/95–1/6/95

The second set of data is based on average daily flow rates for the period 1/3/95–28/12/95 and the frequency distributions of the un-normalised and normalised data are given in fig 3.2. Data were normalised by squaring flow rate and graphed as a normal probability plot in fig 3.3. To meet normality requirements, according to the Ryan-Joiner test, three outliers representing zero flow were removed from the dataset. Hence from fig 3.3:

$$
\begin{aligned}
P(Y \geq 0.01) &= P([Y-\mu] \geq 0.01-0.00646)\\
&= P(Z \geq 1.3732)\\
&= 0.0853
\end{aligned}
$$

where $Z = [Y-\mu]/\sigma$

Consequently there is around a 1 in 12 chance that daily mean flows in Conveyor Tunnel will exceed 100 L/s assuming a normal distribution and an average rainfall (fig 3.4). While there is good correspondence between the frequency of measured daily values > 0.1 cumecs ($n = 22$ ie 7.4% occurrence) and that predicted from normalisation (8.5% occurrence), a much higher figure of 19% was obtained on a truncated dataset derived from continuous monitoring (fig 3.1). However, in reality the flow in Conveyor Tunnel is bimodal with flow rate for a large proportion of time (39%) less than 0.05 cumecs (fig 3.1). Flow is buffered by the storage capacity on Level 18 in Prince Lyell for mine waters which, although limited (6000 m^3) and under mean flow conditions equivalent to only about 21 h holding time, influences flow rate frequency. Hence the observed pattern to flow rate is greatly dependent on the duration over which it is monitored. Daily averaging will tend to dampen the bimodal features of continuous monitoring which essentially reflect whether pumping is either off or on.



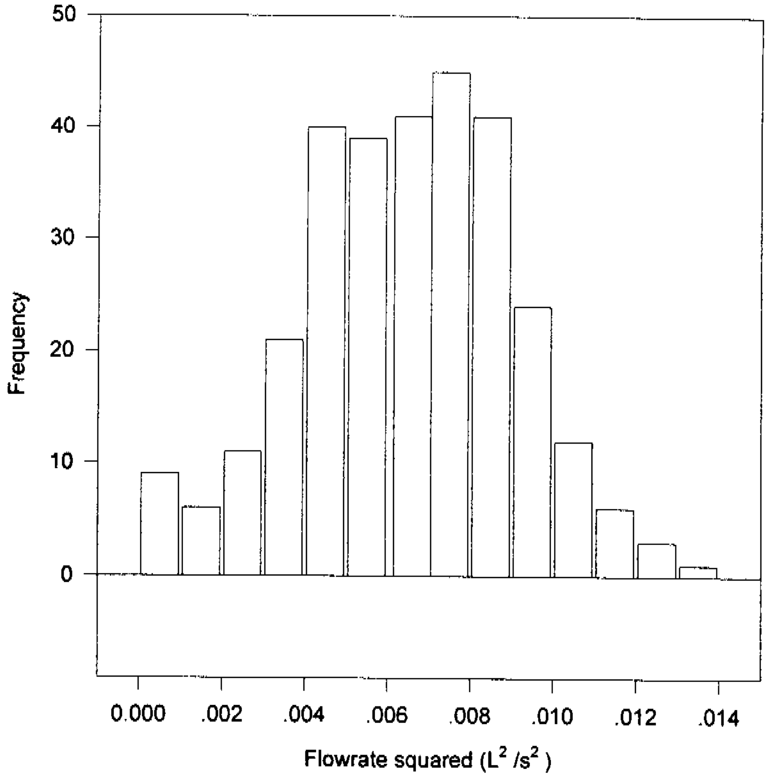


Figure 3.2 Frequency distribution histograms of original (top) and normalised (bottom) average daily flow rates for Conveyor Tunnel (1/3/95–28/12/95)

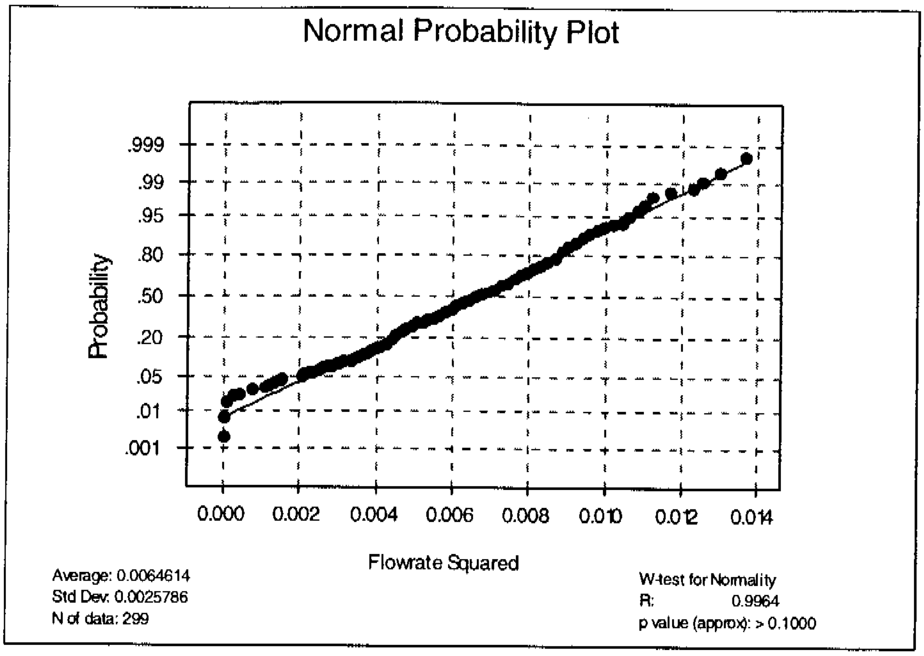


Figure 3.3 Normal probability plot of Conveyor Tunnel mean daily flows (squared)

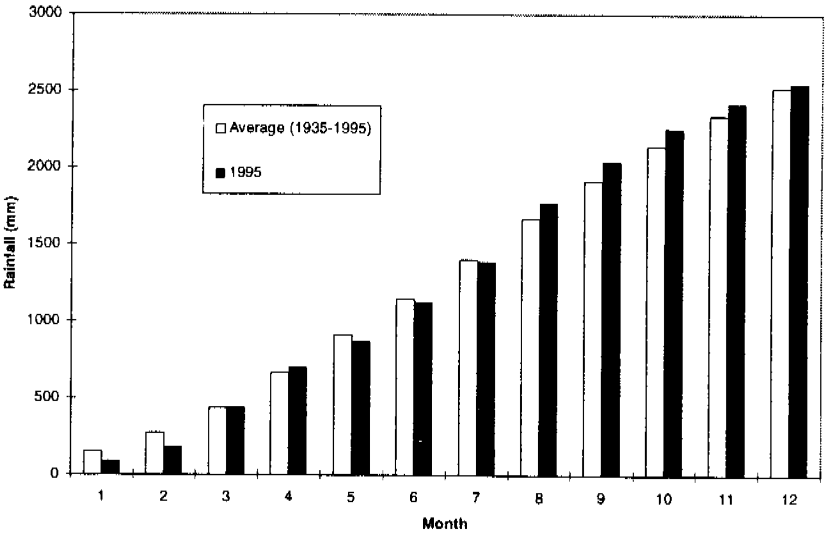


Figure 3.4 Cumulative rainfall at Mount Lyell

4 Scenarios

4.1 Approach

The principal features of the approach taken to predict the impact of remediative measures on the water quality of the Queen and King River systems were that a model so defined should have general application, to account for a variety of rehabilitation actions which might be taken, and, that it should be relatively simple to apply and interpret. In essence, the model consists of two parts: the first deals with dilution of mine effluent by unimpacted river water and the second with speciation predictions based upon the composition of the mix and its chemical equilibria. Speciation was determined using MINTEQA2 Version 3.11. Details of the background to and principles of MINTEQA2 are contained elsewhere (Brown & Allison 1988). Amongst the capabilities of MINTEQA2 are the calculation of saturation indices (SI) to predict the solution and precipitation of minerals based upon ion activity products (IAP) and solubility products (K_{sp}), ie where SI = IAP/ K_{sp}, ion complexation in solution from stability constants, and sorption and exchange according to a variety of assumptions concerning binding sites and ion activities.

The mixing model that was used was based on a single source of acid drainage and two diluents derived from either unimpacted Queen or King water, each of constant composition. The composition of acid drainage was taken as the median concentration of constituents from a combined Conveyor Tunnel and North Lyell Tunnel source (table 2.6) representing around 78% of Cu load from the Mount Lyell lease (table 2.5). Similarly, the compositions of the diluents were also based on median concentrations (table 2.4). Unimpacted waters from the Queen and King River catchments (with the exception of Lake Burbury water) were considered to have the same composition. Mixing of acid drainage with river water was modelled using either a geometric dilution series for the Queen River and King River with the power station off (ie no inflow from Lake Burbury), or in the case of the King with power station on, Lake Burbury providing 80 cumecs (ie the optimum working flow rate for the station) and median flow from other sources.

For speciation modelling, a conservative approach was taken in that the sorption of metals by either naturally occurring suspended matter or precipitates, which were predicted to form from components of the acid drainage, was not invoked. This is discussed further in section 6. The Davies equation was used to calculate ionic activities; temperature in the mixing zone was set at 10°C; and a CO_2 concentration equal to ambient atmospheric partial pressure (ie log $[CO_2] = -3.52$) was taken. The relationship between metal complexing capacity of dissolved organic matter (DOM) and mass was assumed to be as follows: 1 mg C = 1×10^{-6} mole charge.

4.2 Neutralisation of acid drainage

In essence, effective remediation of the Queen and King Rivers will depend upon either, or a combination of, a reduction in the volume of acid drainage entering the river system and/or the neutralisation of the acidity which does. The possibility of diverting all the acid mine drainage to a pipeline for ocean disposal as a remediation option has not been considered here. While some reduction of volume may be feasible by drainage works and capping on selected areas of the lease site (Miedecke 1996), the major effort in countering the impact of acid drainage will be liming so long as mine effluent has direct passage to local creeks and rivers. Alternative technologies such as passive treatment of acid drainage by wetland filters (Miedecke 1996) to increase pH can be regarded for the purposes of modelling as being equivalent to (partial) neutralisation by liming.

The speciation model was first established by considering the proportion of total acid drainage which might be neutralised. Four scenarios equivalent to 8% (current), 65%, 80% and 99% were taken to show not only the effect of rehabilitation on water quality progressively but to allow extrapolation to other values if required. The next stage was to establish pH endpoints for neutralisation and these were set at pH 6.5 and pH 5.5. The permutations of the proportion of total acidity neutralised and pH end-points which were investigated are summarised in fig 4.1.

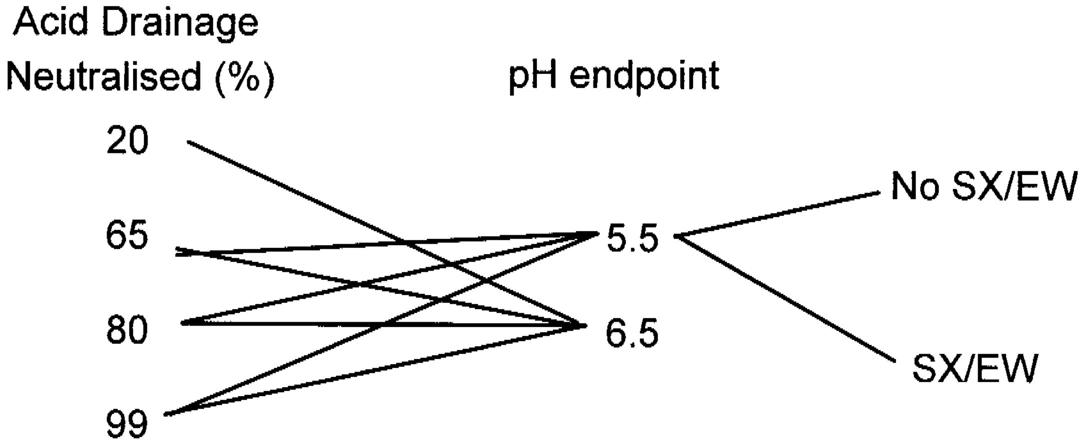


Figure 4.1 Summary of the scenarios modelled

One litre of acid drainage (ie combined West Lyell and Conveyor Tunnel waters of median composition) was subjected to simulated titration with $Ca(OH)_{2(s)}$ using MINTEQA2 (fig 4.2). Constraints were placed on precipitation products (table 4.1) and with the exception of the inclusion of fluorite, antlerite and tenorite, they are similar to those used by EGI (MLMRCL 1995a) for river chemistry modelling. The possibility of an oxyhydroxysulphate of the form $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$ or $Fe_{16}O_{16}(OH)_{10}(SO_4)_3$ as described by Bigham et al (1990) which can be found in acid mine drainage was not taken into account in the absence of thermodynamic data. Similarly, the possible presence of ferrite of the form $CuFe_2O_4$ derived from ferrihydrite as postulated by Hem (1977) was not considered. Table 4.1 also shows the precipitation products present at pH 5.5 and 6.5 and fig 4.3 maps the changes in the mass yields of these products as a function of pH for the titres used.

While the only Fe-containing product was ferrihydrite, Al was precipitated in stages as $AlOHSO_4$, $Al_4(OH)_{10}SO_4$ and gibbsite. However, the only stable Al mineral forming at an equilibrium pH of 5.5 and 6.5 was $Al_4(OH)_{10}SO_4$ and gibbsite respectively. Brochantite was the sole Cu-containing mineral to form at either pH endpoint. Fluoride was removed from solution as fluorite at > pH 5.5 to augment Ca loss to the solid phase as gypsum which was precipitated throughout the pH range. The concentrations of Mn, Zn, Mg, Na, K and Cl in solution were unaffected. The lime requirement to achieve pH 5.5 and 6.5 was 17.7 and 18.2 mmoles $Ca(OH)_2/L$ respectively. The effects of liming on solution composition at equilibrium are summarised in table 4.2. It is important to note, however, that concentrations of Cu, Mn and Zn would likely be lower than that shown because of sorption to charged, pH dependent,oxy-hydroxide surfaces with the effect being more pronounced at pH 6.5. This is discussed further in section 6.

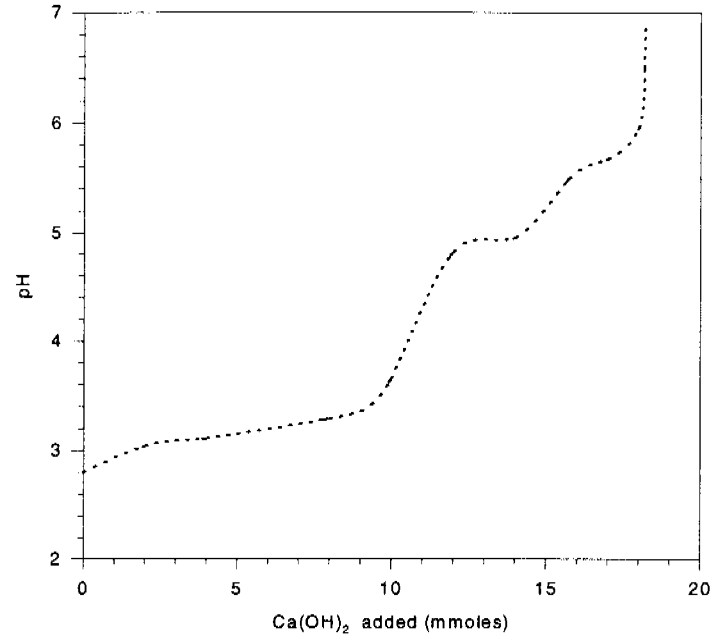


Figure 4.2 Predicted buffer curve for acid drainage titrated with $Ca(OH)_2$

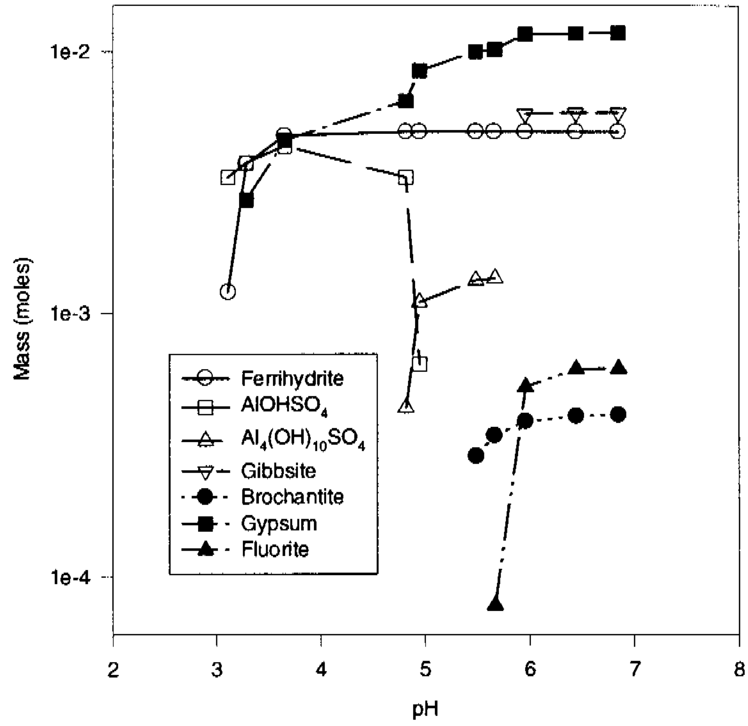


Figure 4.3 Precipitation products from the neutralisation of acid drainage by slaked lime

Table 4.1 Permitted precipitation products at equilibrium resulting from the neutralisation of acid drainage by slaked lime and their presence/absence at pH endpoints

	Presence/Absence	
Precipitating Mineral Phase	**pH 5.5**	**pH 6.5**
$AlOHSO_4.H_2O$	Absent	Absent
$Al_4(OH)_{10}SO_4.10H_2O$	Present	Absent
Ferrihydrite $Fe(OH)_3.3H_2O$	Present	Present
Fluorite CaF_2	Absent	Present
Gibbsite $Al(OH)_3.3H_2O$	Absent	Present
Gypsum $CaSO_4.2H_2O$	Present	Present
$Cu(OH)_2.2H_2O$	Absent	Absent
Antlerite $Cu_3(OH)_4SO_4.4H_2O$	Absent	Absent
Brochantite $Cu_4(OH)_6SO_4.6H_2O$	Present	Present
Tenorite $Cu(OH)_2.H_2O$	Absent	Absent

Table 4.2 Predicted composition (mg/L) of combined Conveyor and West Lyell Tunnel waters after liming to pH 5.5 and 6.5, and the percentage removal of constituents

Composition	**pH**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**F**	**SO_4**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**
Initial	2.8	112	336	6	2	12	25	3110	274	112	157	104	12
pH 5.5	5.5	342	336	6	2	12	25	2006	0.038	112	13.6	31.9	12
% removal pH 5.5	–	54.0	–	–	–	–	–	35.7	100	–	91.4	69.5	–
pH 6.5	6.5	345	336	6	2	12	1.9	1954	0.004	112	0.073	1.3	12
% removal pH 6.5	–	59.0	–	–	–	–	92.4	37.4	100	–	100	98.9	–

4.3 Removal of Cu by SX/EW

At this stage, details of the efficiency of a SX/EW plant to remove Cu are unknown, although Miedecke (1996) has suggested that 80% might be attained. In addition, the pH to which raffinate might be neutralised remains dependent upon operational, economic, and political decisions that have yet to be agreed. In the absence of such data and to permit contrasts to be drawn between possible scenarios, raffinate was considered to contain 15 mg Cu/L which was limed to pH 5.5. Since the neutralisation of raffinate or raw acid drainage to pH 5.5 results in a maximum equilibrium concentration of approximately 32 mg Cu/L (table 4.2), anything less will remain in solution. If SX/EW was to leave a residual Cu concentration of approximately 32 mg Cu/L in solution, this would represent a removal efficiency of 76% based on the median concentration of Conveyor Tunnel discharge and 69% for combined Conveyor and West Lyell Tunnel waters (table 2.6). As will be demonstrated later (see section 6), the model can be used to predict Cu concentration in the river systems based upon a given efficiency of extraction from acid drainage and an endpoint for neutralisation.

The reaction to electrowin Cu is as follows:

Cathode:	$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$	$E_0 = 0.337$
Anode:	$H_2O \rightarrow 1/2\ O_{2(g)} + 2H^+ + 2e^-$	$E_0 = -1.229$
Net:	$H_2O + Cu^{2+} \rightarrow Cu_{(s)} + 1/2\ O_{2(g)} + 2H^+$	$E_0 = -0.892$

Hence in terms of adjusting the predicted composition of the partially neutralised raffinate to some endpoint pH for the model, the decrease in pH resulting from electrolysis is simply compensated by the mole equivalent of Ca^{2+} from liming or, alternatively, the Cu^{2+} which is won is replaced by Ca^{2+} from lime addition.

5 Outcomes

A listing of concentration predictions under all scenarios for pH and total soluble metals is contained in the appendix.

5.1 pH

Model predictions of pH in the Queen and King Rivers with the power station off are summarised for current conditions (fig 5.1) and under the scenarios of variable proportions of acid drainage being neutralised to pH 6.5 (fig 5.2) and pH 5.5 (fig 5.3). Note that in the case of neutralisation of acid drainage to pH 5.5 coupled with SX/EW, pH prediction is identical to that in fig 5.3.

There was little difference at the same dilution between partially neutralising acid drainage to pH 5.5 (fig 5.3) compared with pH 6.5 (fig 5.2). This is not surprising since the overriding effect determining pH is the portion of acid drainage which is not neutralised against the background river water pH of 5.5. For example, 1 mL of acid drainage at pH 2.8 contributes five times more H^+ than 99 times the volume of water at pH 5.5. Hence taking 10% dilution of 99% neutralised acid drainage as an example, the ratio of raw acid drainage: neutralised acid drainage: river water (ie 1:99:990) is influenced least by whether a pH endpoint of 5.5 or 6.5 is used. In addition, as there were no differences in precipitation products between the dilution of partially neutralised acid drainage at pH 5.5 and 6.5 by river water (see section 5.2), the form of the relationship between dilution and equilibrium pH is virtually identical. Anomalous equilibrium pH values were predicted by MINTEQA2 at the two highest dilutions for 99% neutralisation of acid drainage where an endpoint of pH 5.5 was predicted to give values slightly higher than with a pH 6.5 endpoint. This arose because the diluted solutions derived from acid drainage with a pH 5.5 endpoint had a slightly higher ionic strength than at pH 6.5 and hence for the same uncorrected total H^+ concentration, a lower activity of protons was predicted. This problem was reconciled by using pH values based only on a dilution model and it is these which are graphed for the 99% neutralisation treatment at 0.3 and 0.1% dilutions in fig 5.2 and 5.3.

Predicted pH values for median flow in the King River with the power station operating at optimum efficiency (ie 80 cumecs) are given in table 5.1.

Table 5.1 Predicted pH in the King River under median flow with power station on

	pH 5.5 endpoint (% acid drainage neutralised)			pH 6.5 endpoint (% acid drainage neutralised)		
Current	**65**	**80**	**99**	**65**	**80**	**99**
4.47	5.00	5.20	5.91	5.00	5.20	5.91

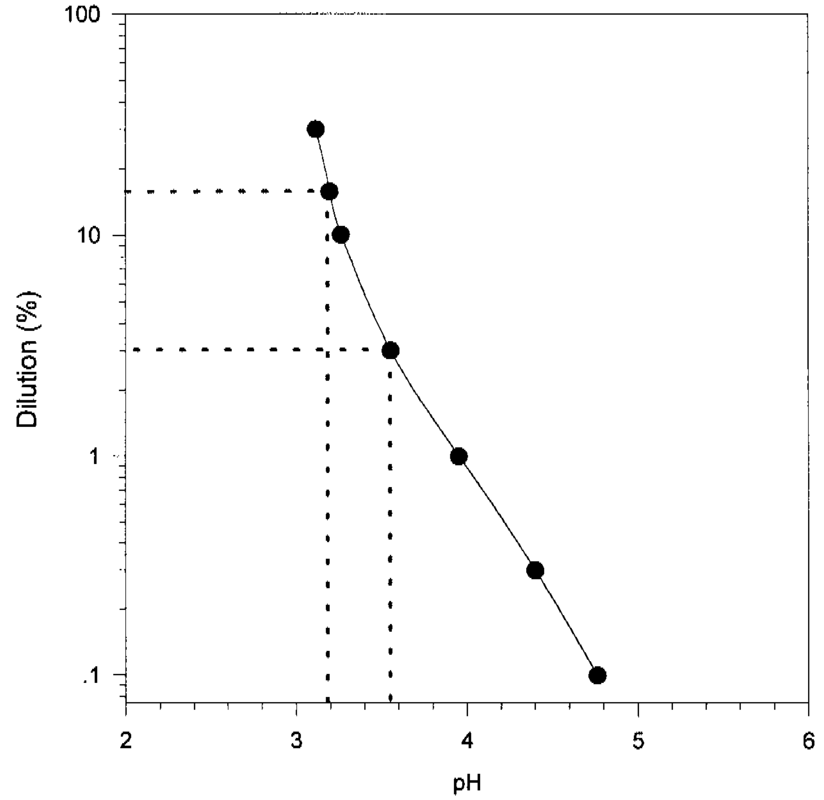
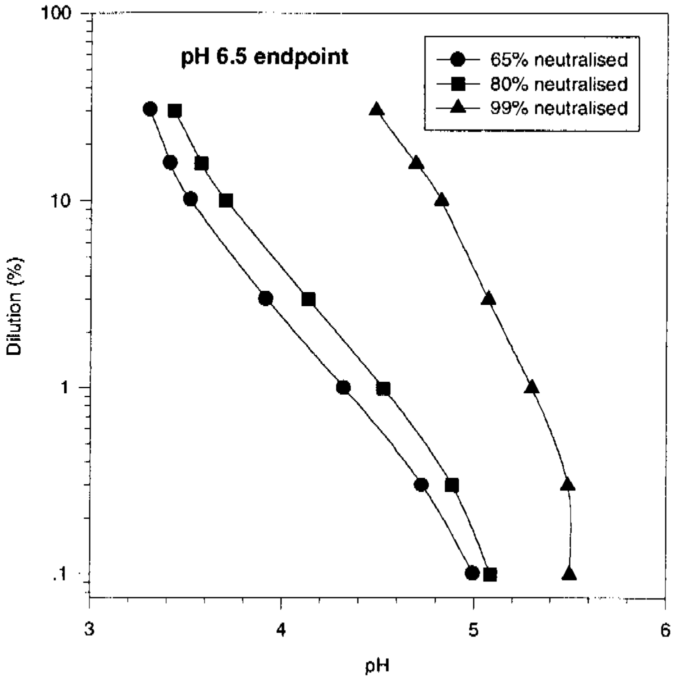


Figure 5.1 Prediction of pH in the Queen and King Rivers (power station off) from variable dilution under current conditions, ie neutralisation of 8% of acid drainage (dashed lines show predicted pH values at median flow in the Queen and King Rivers)

5.2 Copper

5.2.1 Total soluble Cu

The predicted total soluble Cu concentrations in Queen and King River waters (power station off) are summarised in figs 5.4 (current), 5.5 (pH 6.5 endpoint), 5.6 (pH 5.5 endpoint; no SX/EW) and 5.7 (pH 5.5 endpoint; SX/EW) and in table 5.2 for the King River with power station on. For all dilutions under all the modelled scenarios, total soluble Cu behaved conservatively because precipitation was not predicted to occur. No precipitation was observed at the highest observed range of pH values because Cu became sufficiently diluted so that the solubility products for hydroxy-Cu compounds were never exceeded.



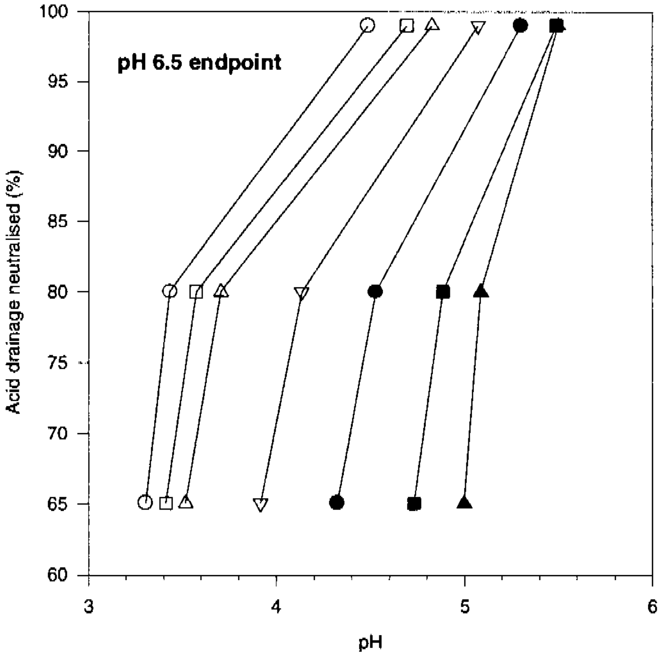
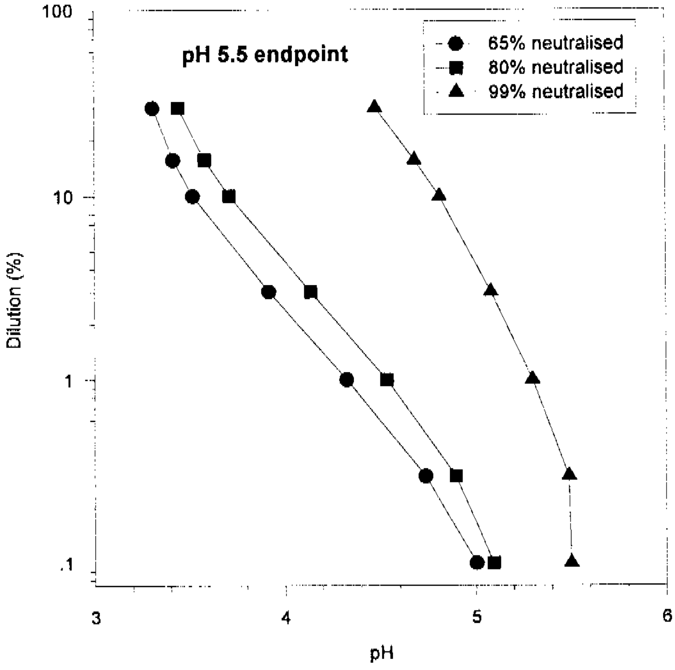


Figure 5.2 Prediction of pH in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.2 (bottom) are from left to right 30, 15.7, 10, 3, 1, 0.3 and 0.1% dilutions of mine drainage



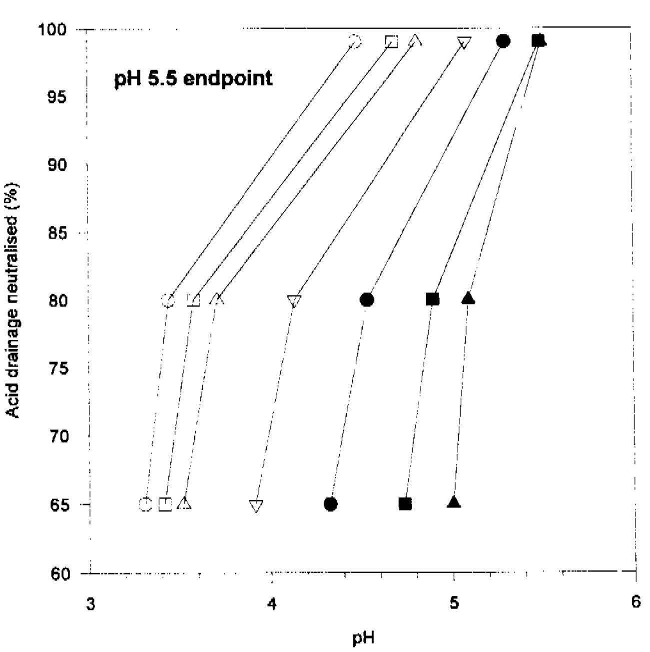


Figure 5.3 Prediction of pH in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 5.5

Note: Treatments shown in fig 5.3 (bottom) are from left to right 30, 15.7, 10, 3, 1, 0.3 and 0.1% dilutions of mine drainage

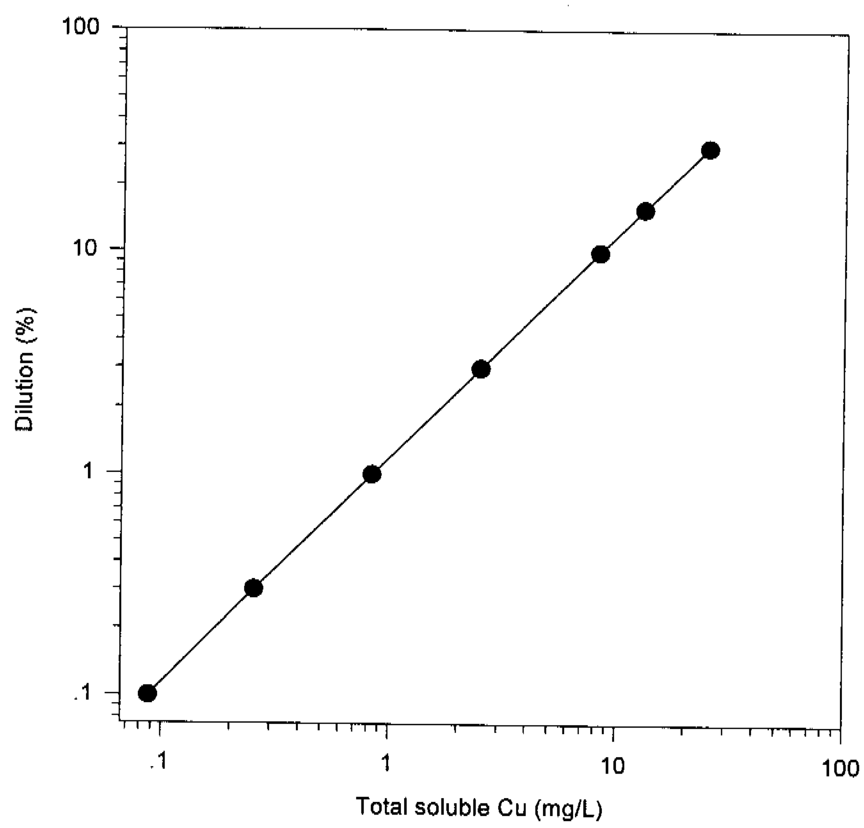
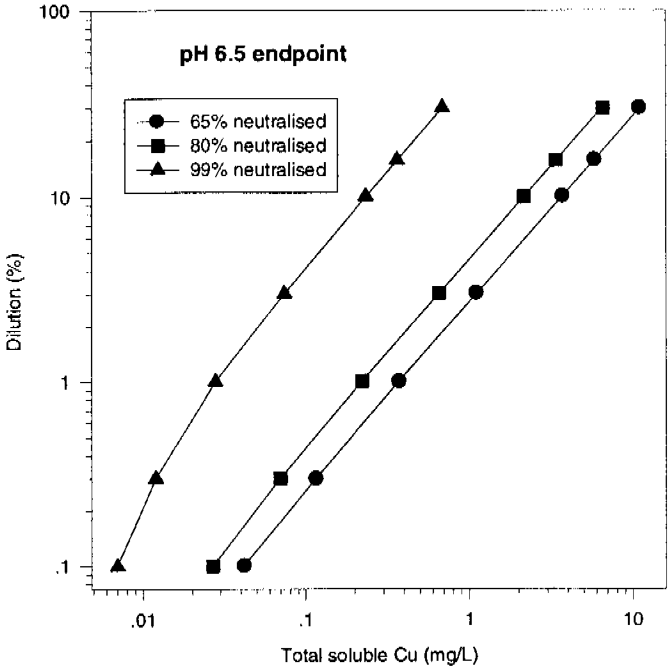


Figure 5.4 Predicted total soluble Cu (mg/L) in the Queen and King Rivers (power station off) from variable dilution under current conditions

Table 5.2 Predicted total soluble Cu (mg/L) in the King River under median flow with power station on

	pH 5.5 endpoint (% acid drainage neutralised)						**pH 6.5 endpoint (% acid drainage neutralised)**		
	no SX/EW			**SX/EW**			**no SX/EW**		
Current	**65**	**80**	**99**	**65**	**80**	**99**	**65**	**80**	**99**
0.225	0.137	0.112	0.080	0.111	0.080	0.042	0.091	0.055	0.010



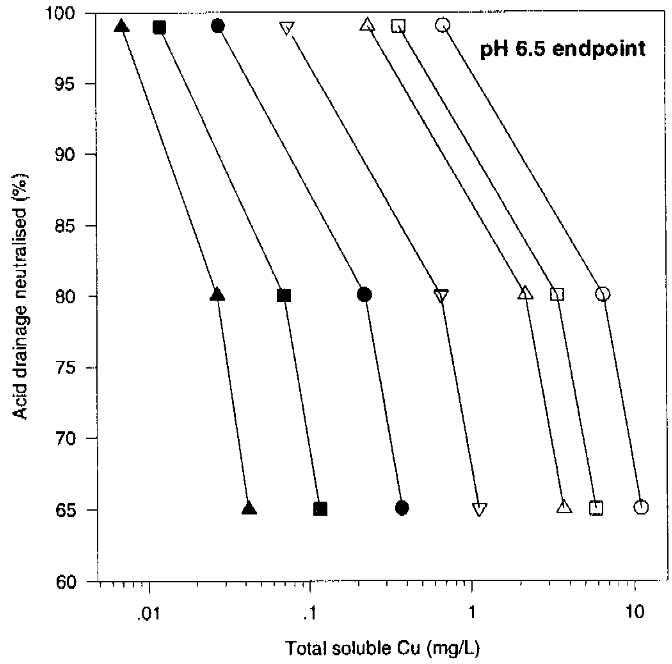
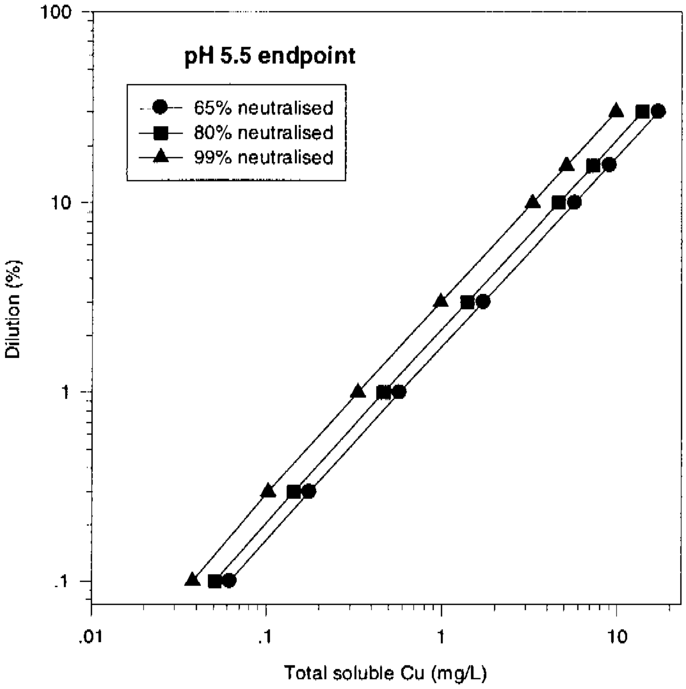


Figure 5.5 Predicted total soluble Cu (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.5 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%



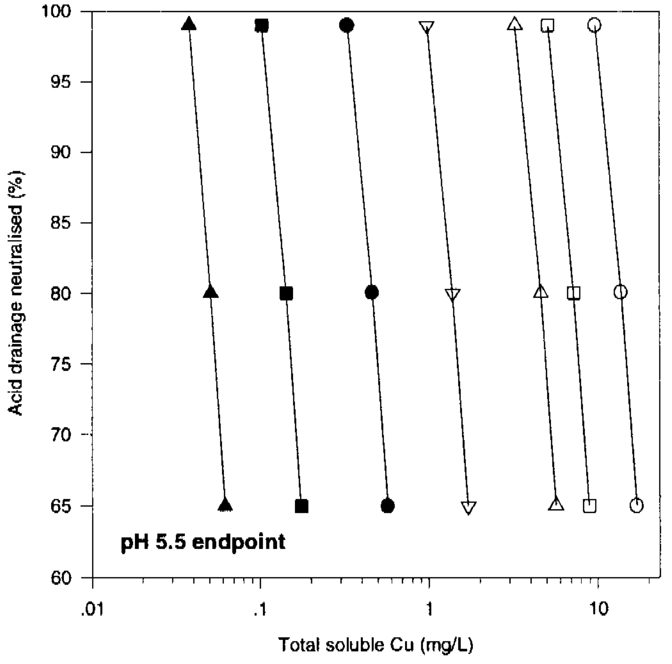
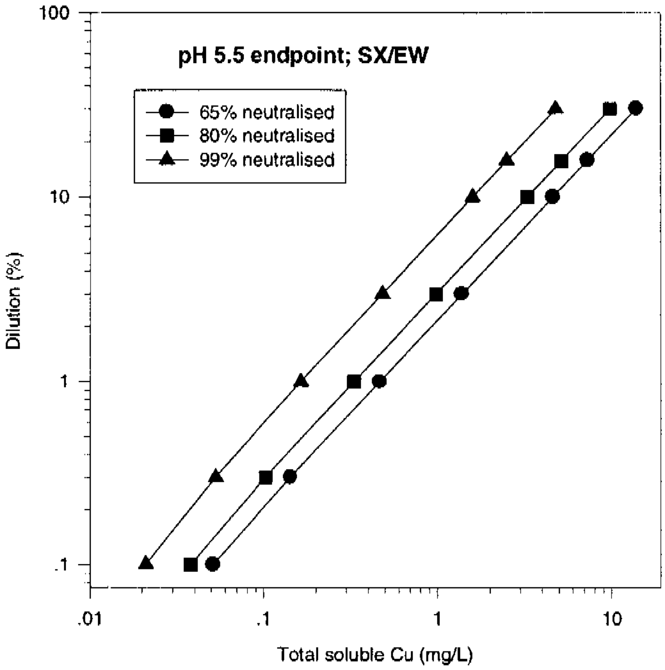


Figure 5.6 Predicted total soluble Cu (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 5.5

Note: Treatments shown in fig 5.6 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%



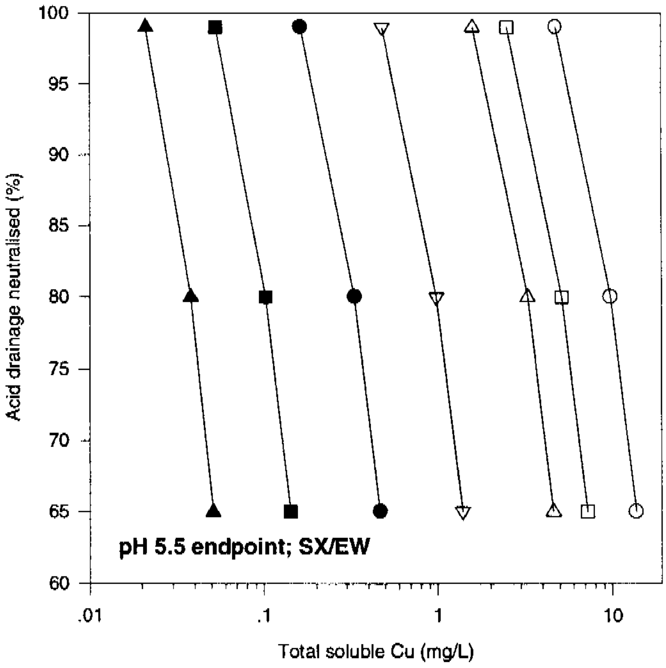


Figure 5.7 Predicted total soluble Cu (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 5.5 coupled with SX/EW

Note: Treatments shown in fig 5.7 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%

5.2.2 Cu speciation

The effects of mixing partially neutralised and raw acid drainage with Queen and King River water (assuming power station off) on the concentration of aqueous Cu^{2+} are summarised for current conditions in fig 5.8 (left), and for endpoints of pH 6.5 and 5.5 in figs 5.9 and 5.10 respectively. In addition, the proportions of dominant soluble Cu species and their change in response to dilution are shown for current conditions in the Queen and King Rivers (fig 5.8 right) and for 65, 80 and 99% neutralisation of acid drainage to either pH 6.5 or 5.5 (fig 5.11). SX/EW and neutralisation to pH 5.5 had only a small effect on Cu speciation compared with no SX/EW at the same neutralisation pH and these differences are summarised in table 5.3. The predicted concentration of Cu^{2+} under median flow in the King River with power station on is described in fig 5.12 and the speciation of total soluble Cu for this scenario in table 5.4.

The principal factors determining speciation in solution under the conditions modelled here are composition, ionic strength and pH. Since neutralisation of acid drainage to either pH 6.5 or 5.5 results in very small differences in pH and ionic strength against a common matrix of diluent, the main factor determining aqueous Cu^{2+} concentration is total soluble Cu and its competition with other metals for complexing ions which, in the case of Cu, are sulphate and dissolved organic matter. Although other Cu-containing complexes are found in solution, including fluoro-, chloro-, carbonato-and hydroxy-species, these collectively for all scenarios and dilutions represented $<1\times10^{-7}$ M Cu and can therefore be ignored.

Under dilute conditions but depending on the proportion of acid drainage that is neutralised (which effectively determines the concentration of total soluble Cu), dissolved organic matter (DOM) assumes significant importance in chelating Cu and reducing the concentration of the cupric ion in the King River (fig 5.11, tables 5.3 & 5.4). This binding capacity of DOM, which is sensitive to pH, is increased when Lake Burbury water of pH 6.2 enters the King (table 5.4) compared with an equivalent dilution of acid drainage, equating to around 0.3%, by diluent at pH 5.5 (fig 5.11). Correspondingly, assuming equal total soluble Cu concentrations and depending on the pH endpoint of neutralisation, between 30–60% of Cu is complexed in river water at pH 5.5 compared with 40–70% when Lake Burbury water (pH 6.2) mixes with King water.

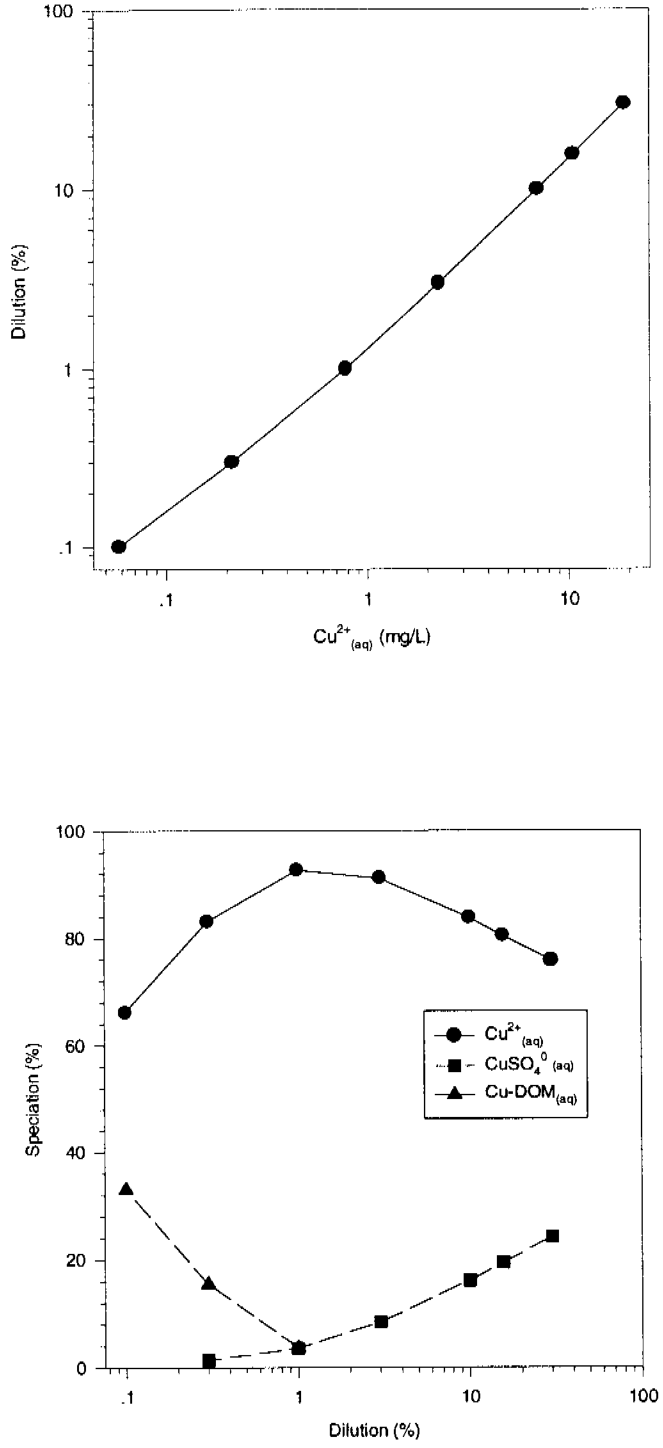
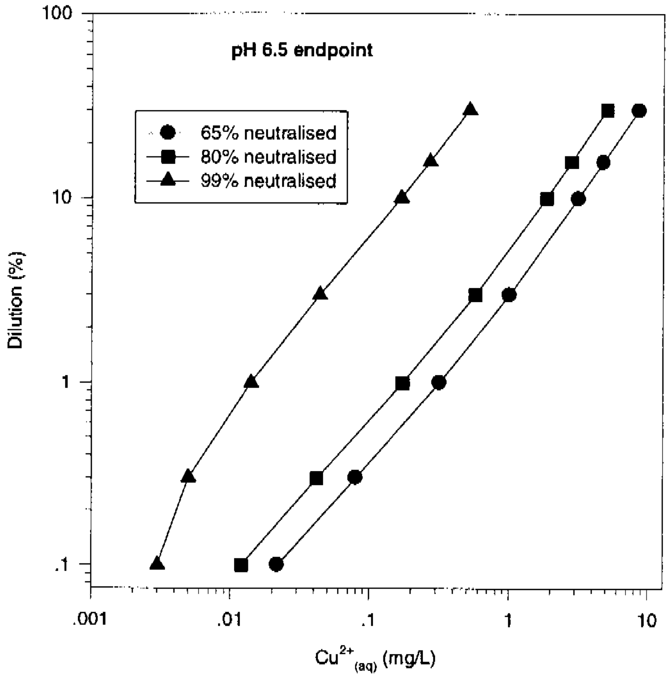


Figure 5.8 Predicted concentration (mg/L Cu) (top) and the proportion of dominant soluble Cu species (bottom) in the Queen and King Rivers (power station off) resulting from variable dilution under current conditions



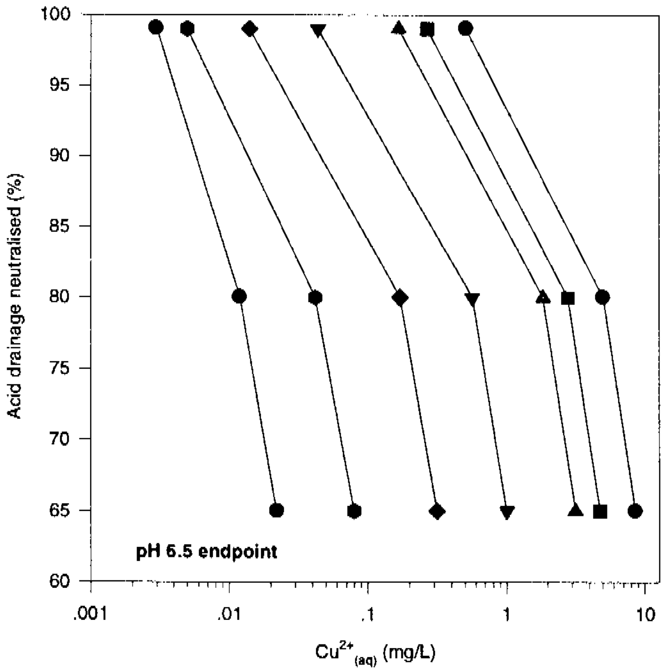
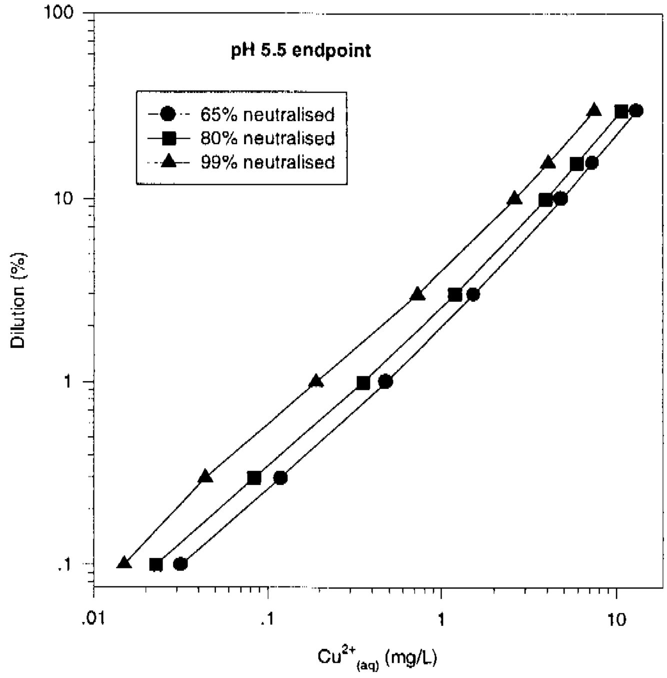


Figure 5.9 Predicted Cu^{2+} (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.9 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%



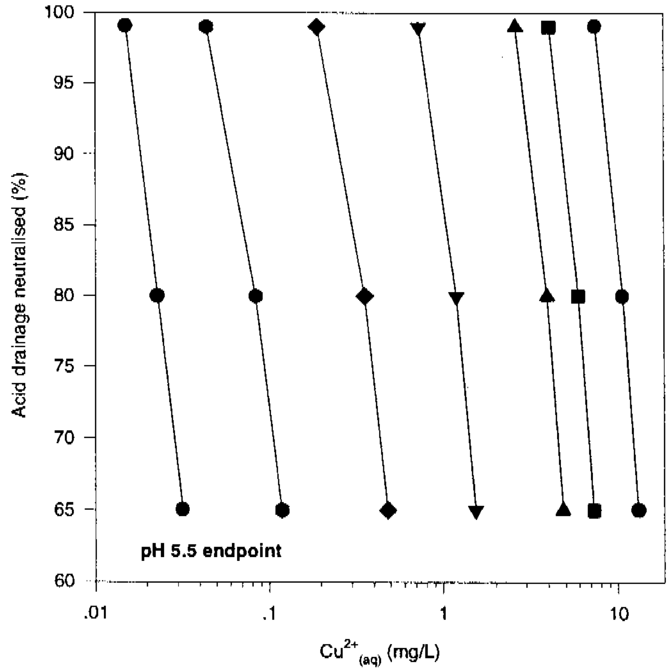


Figure 5.10 Predicted Cu^{2+} (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 5.5

Note: Treatments shown in fig 5.10 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%

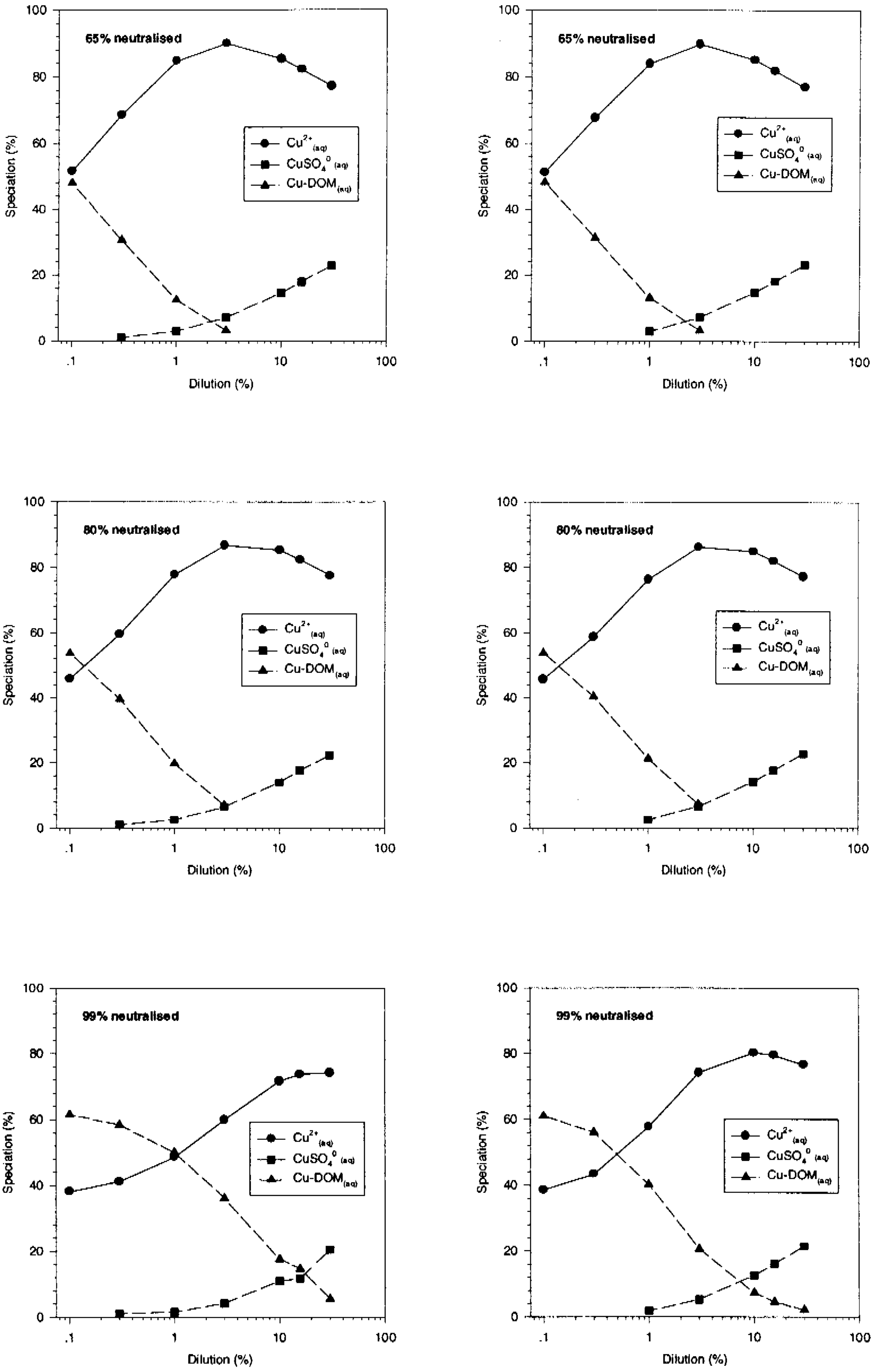


Figure 5.11 The effect of neutralisation endpoint pH 6.5 (left) and 5.5 (right), proportion of acid drainage neutralised and variable dilution on the speciation of total soluble Cu in the Queen and King Rivers (power station off)

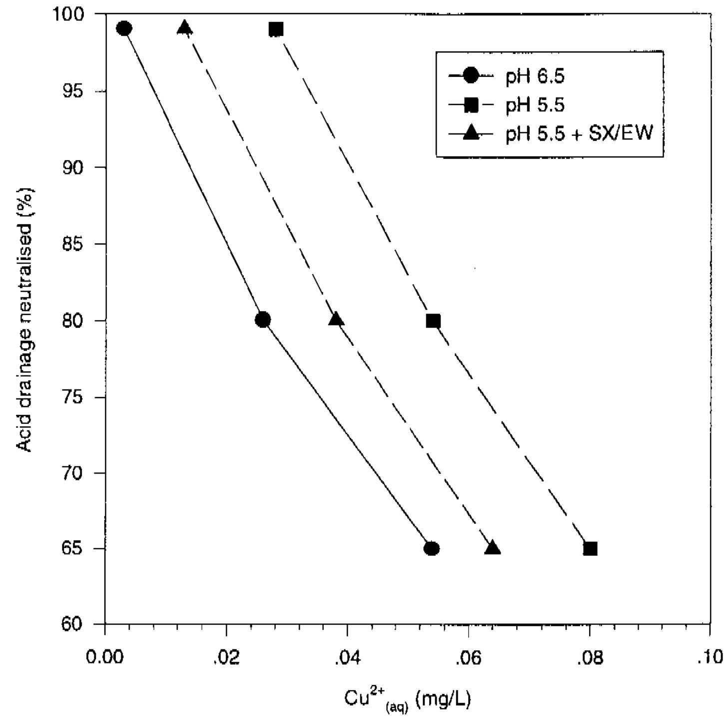


Figure 5.12 Predicted concentration of aqueous Cu2+ (mg/L) in the King River under median flow with power station on

Table 5.3 Effect of SX/EW on predicted Cu speciation at median flow rates in the Queen and King Rivers (power station off)

		% acid drainage neutralised to pH 5.5					
		SX/EW			No SX/EW		
	Species (%)	**65**	**80**	**99**	**65**	**80**	**99**
Queen	Cu^{2+}	81.8	82.0	77.6	81.8	82.0	79.4
	$CuSO_4^0$	18.1	17.6	15.6	18.1	17.6	16.0
	Cu-DOM	–	–	6.7	-	–	4.5
King	Cu^{2+}	89.7	85.6	67.5	89.7	86.2	74.1
	$CuSO_4^0$	7.1	6.4	4.7	7.1	6.5	5.2
	Cu-DOM	3.2	7.9	27.7	3.2	7.3	20.6

Table 5.4 Proportion (%) of total soluble Cu present as dissolved species in the King River under median flow with power station on

	No SX/EW						SX/EW		
	% neutralised to pH 6.5			% neutralised to pH 5.5					
Species	**65**	**80**	**99**	**65**	**80**	**99**	**65**	**80**	**99**
Cu^{2+}	59.1	48.2	29.7	58.5	48.4	34.6	57.6	46.7	32
Cu-DOM	40.1	51.2	69.9	40.6	50.9	64.8	41.6	52.6	67.5

5.3 Aluminium

5.3.1 Total soluble Al

Total soluble Al was conservative throughout the dilution series for all scenarios ie the solubility products of either $AlOHSO_4$, $Al(OH)_{10}SO_4$ or gibbsite were never exceeded. Data are depicted under variable dilution with power station off for current conditions (fig 5.13), and for partial neutralisation of 65, 80 and 99% of acid drainage to pH 6.5 (fig 5.14) and pH 5.5 (fig 5.15). Concentration of Al in the King River with power station on under median flow is shown in table 5.5. Since it is assumed that SX/EW does not lead to any change in total soluble Al, the dilution trend is identical to concentration predictions given in fig 5.15 and table 5.5 for partial neutralisation to pH 5.5.

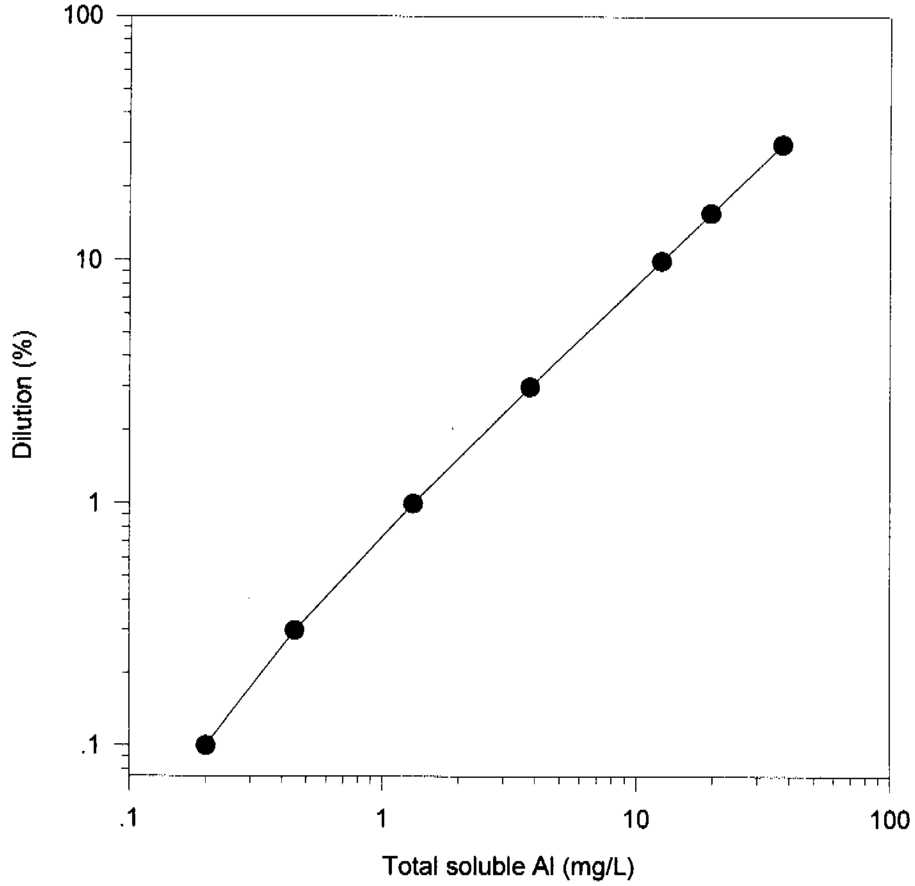
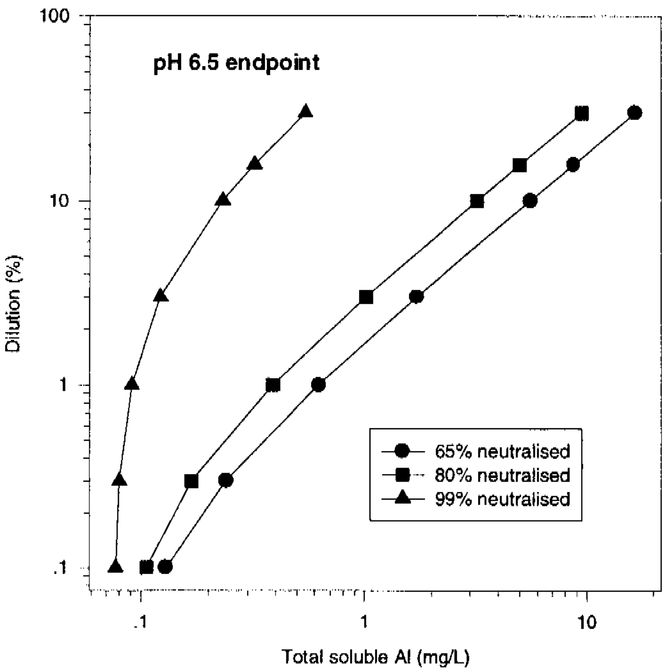


Figure 5.13 Predicted total soluble Al (mg/L) in the Queen and King Rivers (power station off) from variable dilution under current conditions

Table 5.5 Predicted total soluble Al (mg/L) in the King River under median flow with power station on

	pH 5.5 endpoint (% acid drainage neutralised)			pH 6.5 endpoint (% acid drainage neutralised)		
Current	**65**	**80**	**99**	**65**	**80**	**99**
0.357	0.170	0.121	0.058	0.150	0.096	0.027



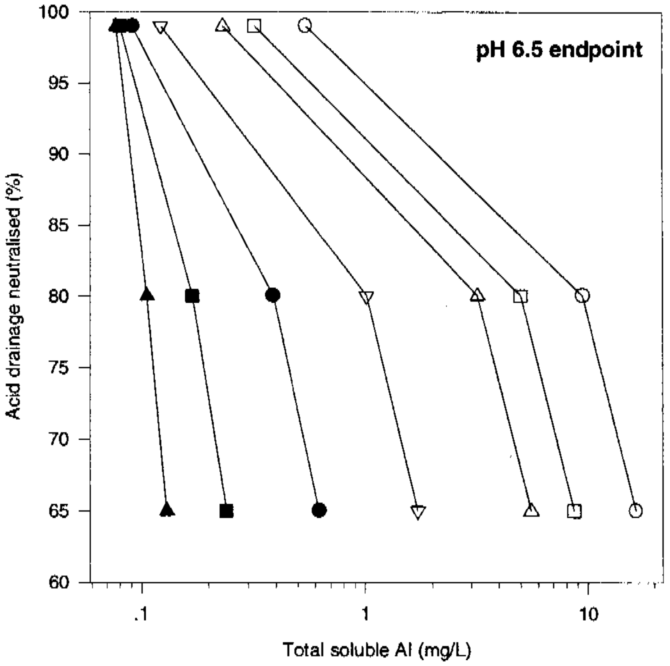
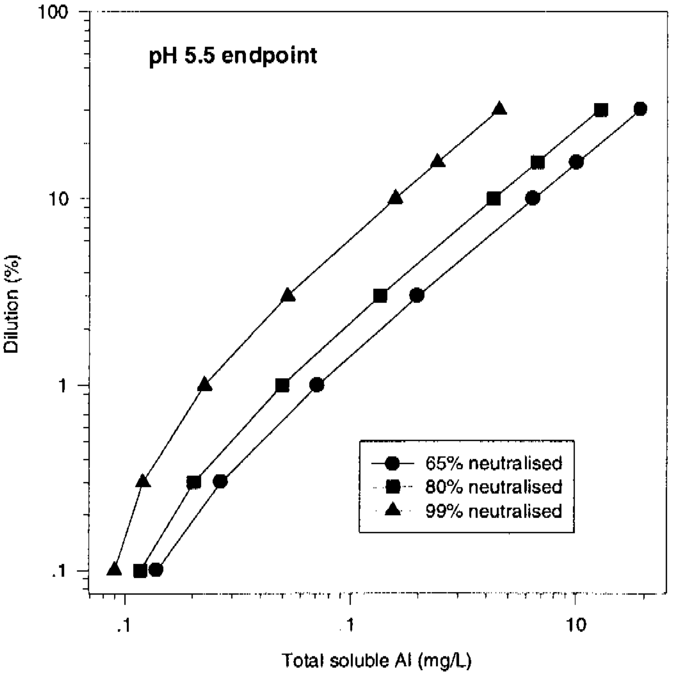


Figure 5.14 Predicted total soluble Al (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.14 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%



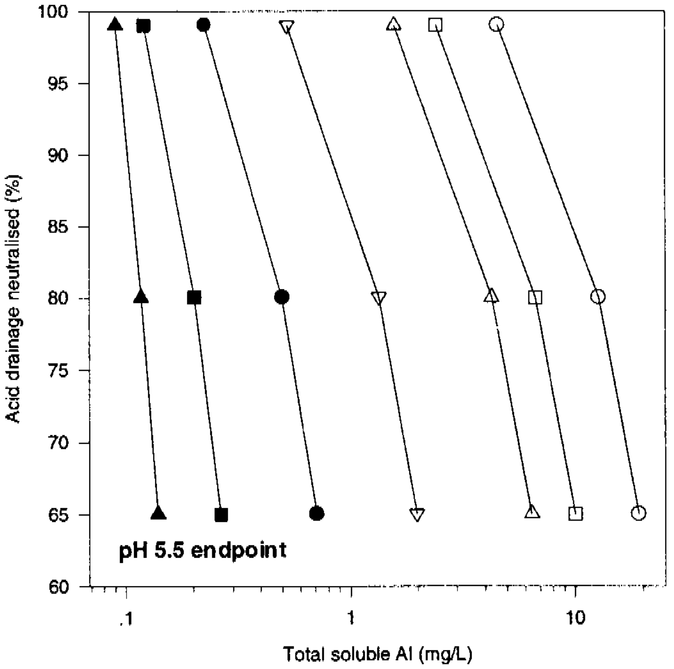


Figure 5.15 Predicted total soluble Al (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 5.5

Note: Treatments shown in fig 5.15 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%

5.3.2 Al speciation

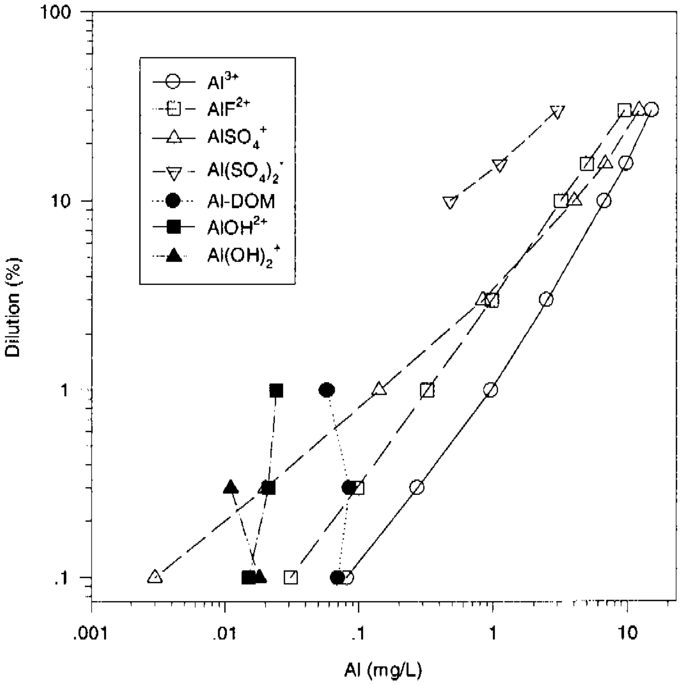
Aluminium can take a variety of forms in solution and these are shown for the Queen and King Rivers with power station off in figs 5.16 (current): 5.17 (pH 6.5 endpoint) and 5.18 (pH 5.5 endpoint; no SX/EW). There were no predicted changes under median flow conditions in the Queen River either in the profile of Al species or their predicted concentrations from conducting SX/EW (compared with no SX/EW and neutralisation of acid drainage to pH 5.5), and, similarly, only minor changes predicted in Al chemistry in the King River (table 5.6) with the power station off. A comparison of the scenarios with the power station on is provided in table 5.7 with the most marked influences on Al speciation being determined by the proportion of acid drainage neutralised and the choice of pH endpoint.

As a strong Lewis acid, the hexaaqua Al species forms stable ion-pairs with strong Lewis bases which in the context of the composition of acid drainage from Mount Lyell result in fluoro-aluminium complexes, principally the mono- (ie AlF^{2+}) but including the di- (ie AlF_2^+) and tri- (ie $AlF_{3\,(aq)}$) species. There is also the possibility of mixed complexes of the form $Al(OH)_xF_yL_z$ (where L represents an organic ligand) being found in waters (Sanjuan & Michard 1987) but in the absence of thermodynamic data their occurrence was not taken into account.

An increase in pH results in the hydrolysis of hexaaqua Al^{3+} with the formation of mono-, di- and tri-hydroxy species (ie $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_{3\,(aq)}$) which will extend some buffering to pH change. Polymeric species such as hydrated $Al_2(OH)_2^{4+}$ and $Al_7(OH)_{16}^{5+}$ may also form as a precursor to the precipitation of $Al(OH)_3$ (Deighton & Goodman 1995) but the latter are unlikely to assume relatively high activities in solution and were not considered to be important in the speciation model.

Sulphate, being a strong Lewis base, also forms ion pairs with Al of which $AlSO_4^+$ is the most common in the mixtures of acid drainage with river water diluent. Under relatively less dilute, high ionic strength conditions, the anion $Al(SO_4)_2^-$ is found.

In the model, the general effect of dilution is to increase the relative importance of DOM as a complexer of Al and, with the consequential asymptotic increase in pH, to favour the formation of hydroxy-aluminium species (as described above and shown in either figs 5.16, 5.17 or 5.18). Liming to pH 6.5 compared with 5.5 gives rise to strong contrasts in Al speciation (figs 5.17 & 5.18). Since neutralising acid drainage to pH 6.5 causes the precipitation of fluorite (see section 4.2), fluoro-aluminium complexes are more dominant in river water receiving the more acid effluent. This is an important finding because if Al bioavailability was to be the most limiting factor to the establishment and survival of keystone species in either the King or Queen Rivers, the attenuation of Al toxicity by F would require appraisal. This is discussed further in section 6.



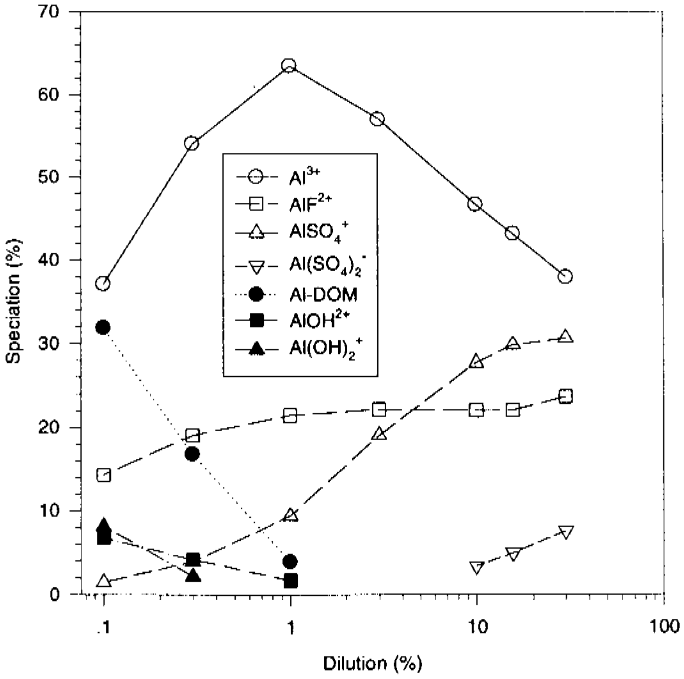


Figure 5.16 Predicted concentration (mg/L Al) (top) and the proportion of dominant soluble Al species (bottom) in the Queen and King Rivers (power station off) resulting from variable dilution under current conditions

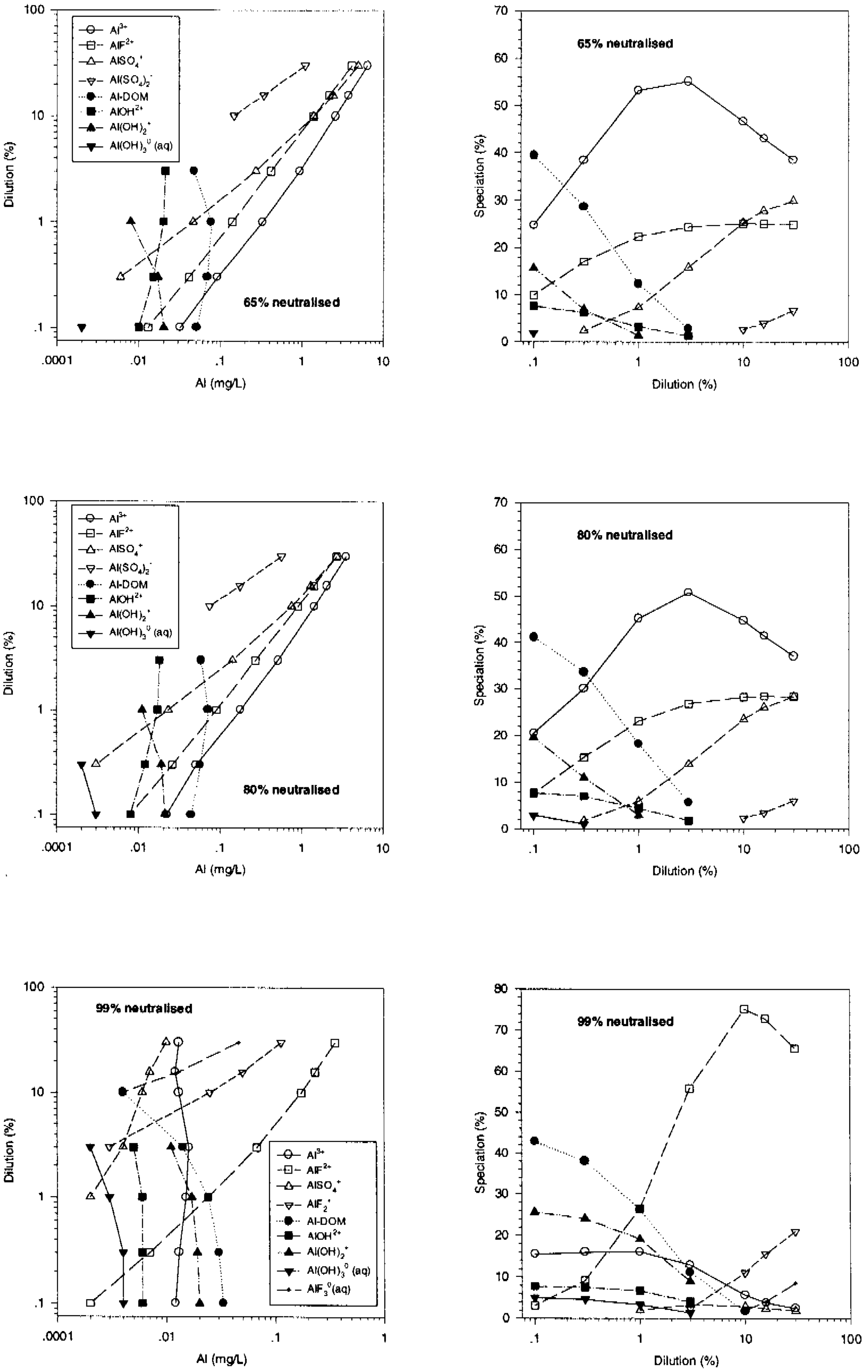


Figure 5.17 The effects of a neutralisation endpoint of pH 6.5, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L Al) (left) and proportion (right) of soluble Al species in the Queen and King Rivers (power station off)

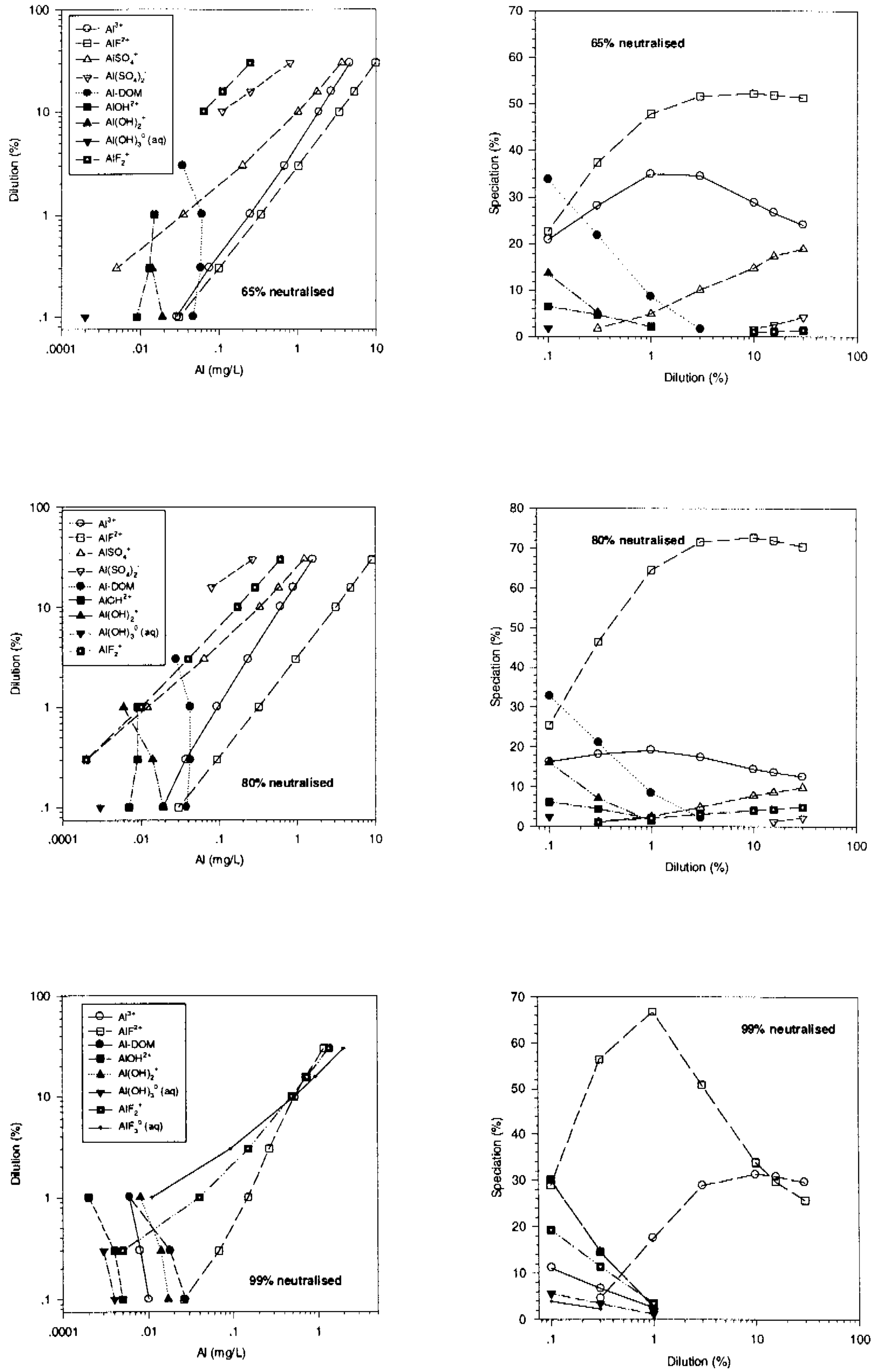


Figure 5.18 The effects of a neutralisation endpoint of pH 5.5 without SX/EW, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L Al) (left) and proportion (right) of soluble Al species in the Queen and King Rivers (power station off)

Table 5.6 Effect of SX/EW on predicted Al speciation at median flow rates in the King River (power station off) with acid drainage neutralised to pH 5.5

	SX/EW			No SX/EW		
Species (%)	**65**	**80**	**99**	**65**	**80**	**99**
Al^{3+}	34.5	17.2	–	34.6	17.4	–
AlF^{2+}	51.6	71.6	50.6	51.6	71.6	50.8
AlF_2^+	–	3.0	28.7	–	3.0	28.8
$AlF_{3\,(aq)}$	–	–	17.8	–	–	17.7
$AlSO_4^+$	10.0	4.8	–	10.1	4.8	–
Al-DOM	1.8	2.2	–	–	2.1	–

Table 5.7 Dissolved Al species (% of total soluble Al) in the King River under median flow with power station on as influenced by SX/EW and the percentage of acid drainage neutralised

	No SX/EW						SX/EW		
	% neutralised to pH 6.5			% neutralised to pH 5.5					
Species	**65**	**80**	**99**	**65**	**80**	**99**	**65**	**80**	**99**
Al^{3+}	29.3	20.5	7.3	20.5	11.6	3.8	20.1	11.3	3.7
$AlOH^{2+}$	6.1	6.6	6.2	4.3	3.8	3.1	4.3	3.7	3.0
$Al(OH)_2^+$	8.6	14.2	35.0	6.2	8.5	16.8	6.2	8.4	16.8
$Al(OH)_{3\,(aq)}$	–	1.8	11.8	–	1.1	5.5	–	1.1	5.5
AlF^{2+}	20.1	18.9	9.9	42.4	51.5	51.3	42.4	51.2	50.3
AlF_2^+	–	–	–	–	2.2	6.6	–	2.2	6.6
$AlSO_4^+$	1.5	1.1	–	1.1	–	–	1.1	–	–
Al-DOM	33.5	36.8	29.3	24.0	20.6	11.9	24.6	21.4	13.0

5.4 Manganese

5.4.1 Total soluble Mn

Since Mn is not precipitated chemically from solution below a pH of around 7.8, there was no difference in the composition of partially neutralised acid drainage between the pH 6.5 and 5.5 endpoints. Likewise, the acidic background pH of the natural waters meant that total soluble Mn remained in solution and behaved conservatively and identically under all the scenarios which were modelled and, consequently, the change in total soluble Mn with dilution can be described as a single relationship (fig 5.19).

5.4.2 Mn speciation

Manganese chemistry in the Queen and King Rivers under the modelling scenarios is dominated by the hexahydrated Mn^{2+} cation which accounts for around 80% (at 30% dilution) to 99% (at 0.1% dilution) of total soluble Mn with the remainder present as the zero-charged $MnSO_{4(aq)}$ ion-pair. With an increasing volume ratio of diluent : acid drainage, the proportion of the free Mn^{2+} increases with the effect of either proportion of acid drainage neutralised, pH endpoint for neutralisation or SX/EW being small and of minor importance (table 5.8).

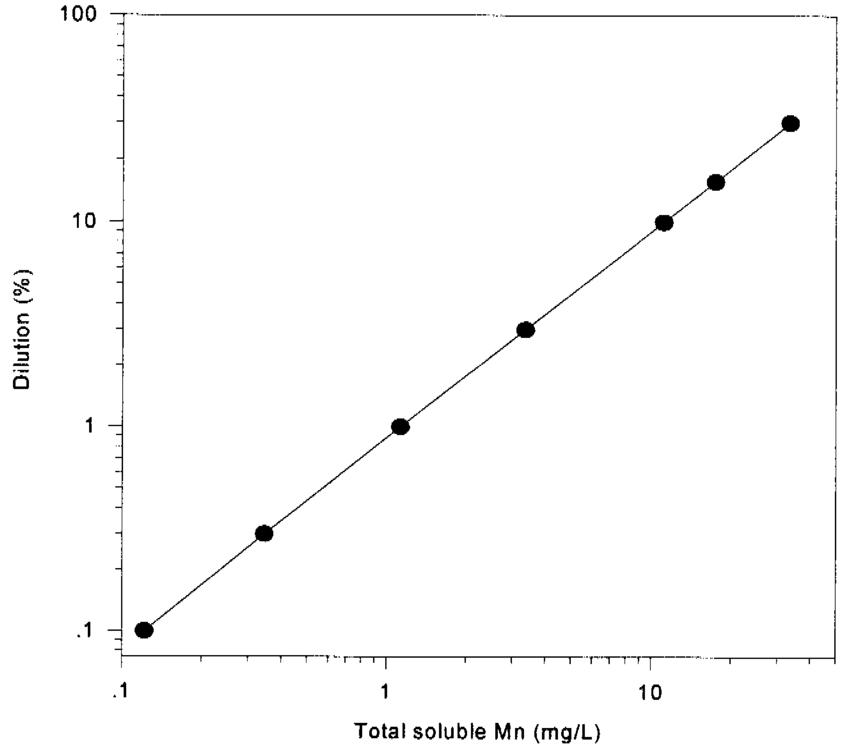


Figure 5.19 Predicted total soluble Mn concentration (mg/L) as a function of treated + untreated acid drainage dilution in the Queen and King Rivers

Table 5.8 Proportion (%) of total soluble Mn as Mn^{2+} under various scenarios in the Queen and King Rivers

Treatment		Dilution (%)		
		15.7	**3**	**0.3**
Current		83.5	92.9	98.5
pH 6.5 endpoint	65% AD neutralised	84.8	93.9	98.9
	80% AD neutralised	85.3	94.2	98.9
	99% AD neutralised	86.0	94.6	99.0
pH 5.5 endpoint	65% AD neutralised	84.6	93.8	98.9
	80% AD neutralised	85.0	94.1	98.9
	99% AD neutralised	85.8	94.5	99.0
pH 5.5 endpoint; SX/EW	65% AD neutralised	84.6	93.8	98.9
	80% AD neutralised	85.0	94.1	98.9
	99% AD neutralised	85.8	94.5	99.0

Note: Acid drainage (AD); 15.7, 3, and 0.3% dilutions represent approximations to median flow in the Queen River, King River with power station off, and King River with power station on respectively.

5.5 Iron

5.5.1 Total soluble Fe

The effects of dilution on total soluble Fe in the Queen and King Rivers with power station off are summarised for current conditions (fig 5.20) and for 65, 80 and 99% neutralisation of acid drainage to pH 6.5 (fig 5.21). For simplicity and in the absence of Eh data, it is assumed for all scenarios that Fe is completely oxidised to the ferric form which allows $Fe(OH)_3$ in the form of ferrihydrite to be precipitated. In this manner, speciation modelling predicts that on mixing raw and neutralised acid drainage with river water, ferrihydrite is precipitated throughout the dilution range. The only exception to this for the scenarios studied is if 99% neutralised acid drainage (either to pH 5.5 or 6.5) is diluted to ≤1% whereupon the solubility product for ferrihydrite is not exceeded. Because liming acid drainage to pH 6.5 leads to a total Fe equilibrium concentration of 0.004 mg/L compared with 0.038 mg/L at pH 5.5, differences in the flux of Fe to the river systems between these pH endpoints for partially neutralised acid drainage are insignificant to that provided by raw acid drainage (ie 274 mg/L). Consequently, fig 5.21 can be used to estimate the effect of dilution for a pH 5.5 endpoint of neutralisation and since SX/EW is assumed to have no effect on Fe concentration, the same relationship (fig 5.21) holds for the latter. Concentration of total soluble iron for median flow in the King River with power station on is given in table 5.9.

Table 5.9 Total soluble Fe (mg/L) in the King River at median flow with power station on

	% acid drainage neutralised		
Current	**65**	**80**	**99**
0.366	0.133	0.076	0.012

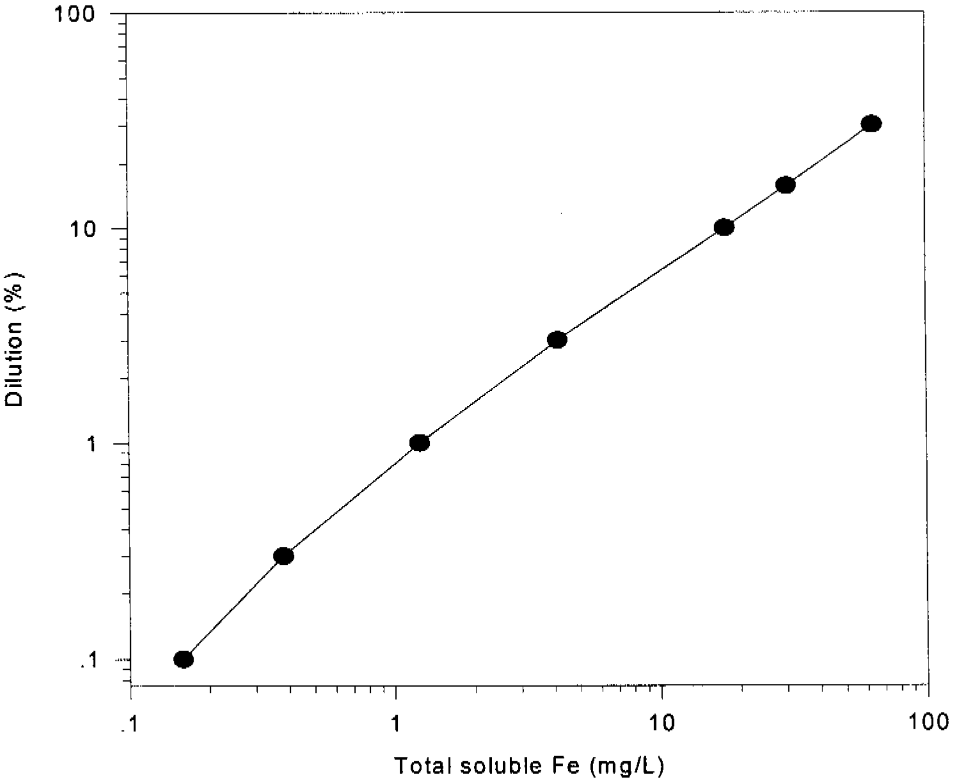
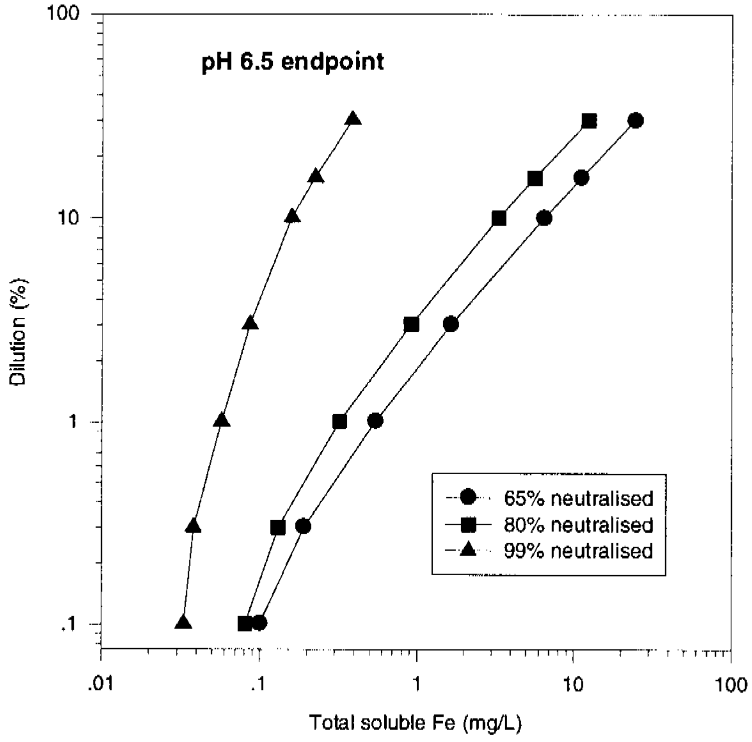


Figure 5.20 Predicted total soluble Fe (mg/L) in the Queen and King Rivers (power station off) from variable dilution under current conditions



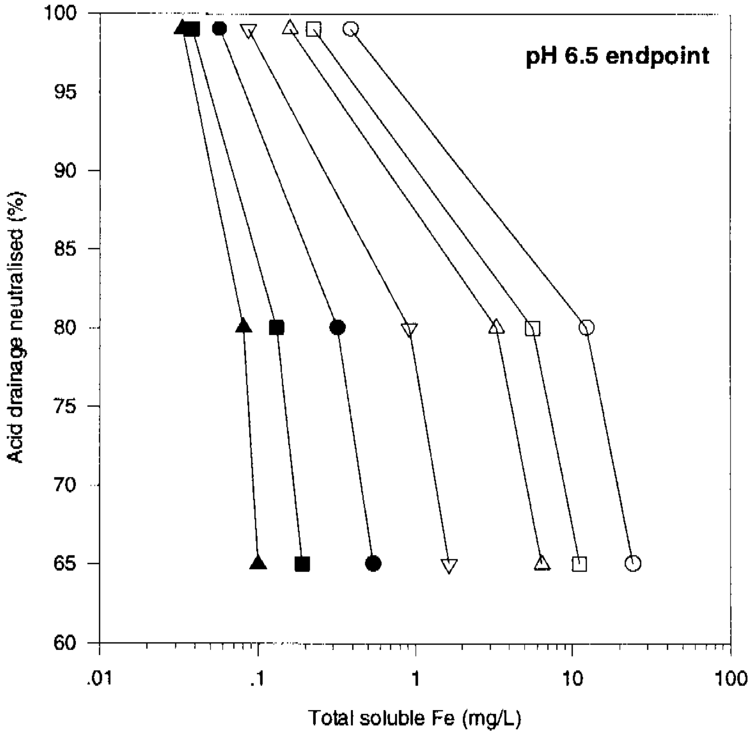


Figure 5.21 Predicted total soluble Fe (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.21 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%

5.5.2 Fe speciation

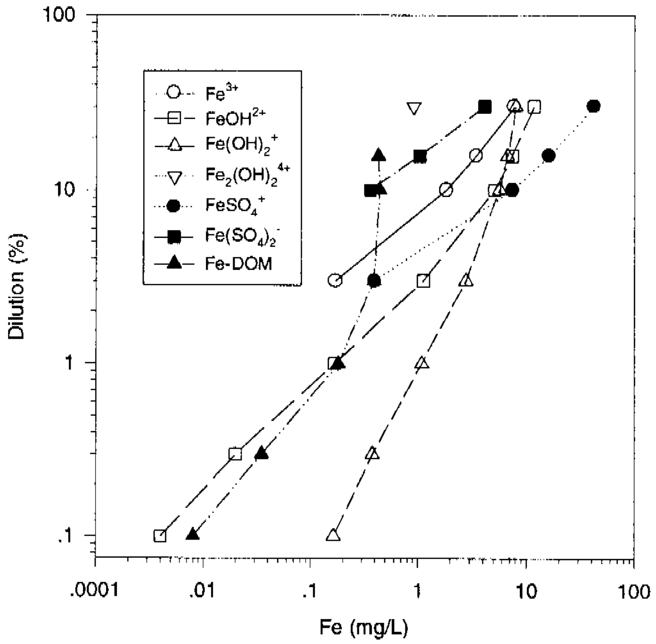
As a hard Lewis acid, ferric ion speciates with hydroxide, sulphate and fluoride, and is complexed by dissolved organic matter (figs 5.22, 5.23 & 5.24). For the majority of conditions described by the tested scenarios, the chemistry of Fe (III) in solution is dominated by the formation of hydroxy-complexes in hexa-coordination with water principally as $Fe(H_2O)_4(OH)_2^+$ which is favoured over $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5(OH)^{2+}$ with an increase in pH (ie more dilute conditions). Where raw acid drainage is more concentrated (fig 5.22), bidentate ferric-hydroxy complexes may form (ie $Fe_2(OH)_4^{4+}$) in conjunction with sulphato-complexes whereupon $FeSO_4^+$ becomes the dominant soluble ferric species (figs 5.23 & 5.24). Under all scenarios, the importance of DOM as a complexer of Fe is secondary to that of hydroxide.

For any given dilution, there is only a relatively small effect of neutralisation endpoint as a factor influencing either speciation of ferric iron or concentration of individual forms (figs 5.23 & 5.24). The main difference to be found arises from the higher concentration of total soluble F in solutions derived from neutralising acid drainage with pH 5.5 compared with pH 6.5 which favours the formation of the FeF^{2+} ion-pair (fig 5.24). However this fluoro-ferric complex is relatively minor in importance and is not found to any appreciable extent at <10% dilution.

A summary of speciation in the King River under median flow with power station on is given in table 5.10.

Table 5.10 Dissolved Fe (III) species (% of total soluble Fe) in the King River under median flow with power station on as influenced by SX/EW and the percentage of acid drainage neutralised

		No SX/EW						SX/EW		
		% neutralised to pH 6.5			% neutralised to pH 5.5					
Species	**Current**	**65**	**80**	**99**	**65**	**80**	**99**	**65**	**80**	**99**
$FeOH^{2+}$	3.9	1.8	1.2	–	1.8	1.2	–	1.7	1.1	–
$Fe(OH)_2^{2+}$	87.9	93.8	95.8	98.3	93.9	96.0	98.4	93.8	95.9	98.3
Fe-DOM	8.1	4.3	2.9	–	4.3	2.7	–	4.4	2.9	–



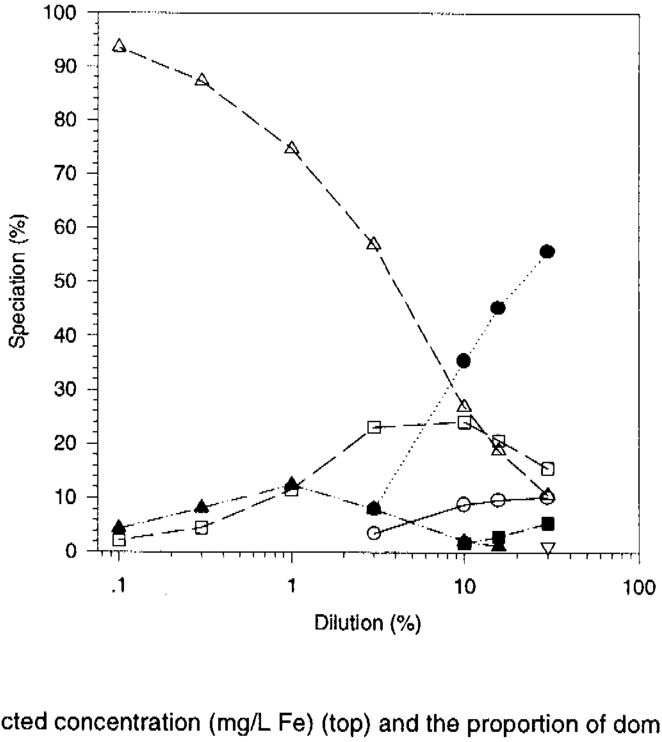


Figure 5.22 Predicted concentration (mg/L Fe) (top) and the proportion of dominant soluble Fe(III) species (bottom) in the Queen and King Rivers (power station off) resulting from variable dilution under current conditions

5.6 Fluoride

5.6.1 Total soluble fluoride

Total soluble fluoride behaved conservatively under all the scenarios but because F is precipitated as fluorite at pH 6.5, and not pH 5.5, the proportion of acid drainage which is neutralised assumes importance only at the former pH. Consequently, and because only 8% of total acid drainage is currently being neutralised to pH 6.5, there is little difference in total soluble fluoride between that predicted under current conditions and if pH 5.5 is used as an endpoint (fig 5.25 & table 5.11). The effect of the proportion of acid drainage neutralised to pH 6.5 is shown in fig 5.26 for the Queen and King Rivers with power station off and table 5.11 summarises the concentration of total soluble fluoride in the King River with power station on under the different scenarios. The use of SX/EW has no effect on total soluble fluoride concentration.

5.6.2 Fluoride speciation

Under all the conditions which were modelled (figs 5.27, 5.28 & 5.29), F chemistry in the Queen and the King Rivers is dominated by the formation of positively-charged fluoro-aluminium complexes, principally the mono-fluoro form (ie AlF^{2+}). In addition, high F:Al ratios which occur when 99% of acid drainage is neutralised to pH 5.5 (fig 5.29), favour the speciation of di-, tri- and tetra-fluoro aluminium given that ionic strength is relatively high (ie ≥ 3% dilution of raw + neutralised acid drainage). Of lesser importance is the formation of the mono-fluoro iron (III) complex whose presence in significant concentration is limited to low pH solutions derived from a combination of low dilution (≥ 10%) and the addition of ≥ 20% raw acid drainage to provide a relatively high Fe input (figs 5.27, 5.28 & 5.29).

In general, a decrease in the ionic strength of solutions, in this case either from neutralising a greater proportion of raw acid drainage or in combination with dilution of acid drainage by river water, does not favour the formation of ion-pairs because of the tendency predicted by chemical thermodynamics of the activity coefficients of free ions in solution to approach unity. Consequently, the concentration of fluoride ion (ie F^-) and its relative abundance as a proportion of total soluble F in solution at a given dilution increases with a decrease in ionic strength (figs 5.28 & 5.29 & table 5.12).

Table 5.11 Predicted total soluble F (mg/L) in the King River under median flow with power station on

		pH 6.5 endpoint (% acid drainage neutralised)		
Current	**pH 5.5 endpoint**	**65**	**80**	**99**
0.053	0.058	0.023	0.015	0.005

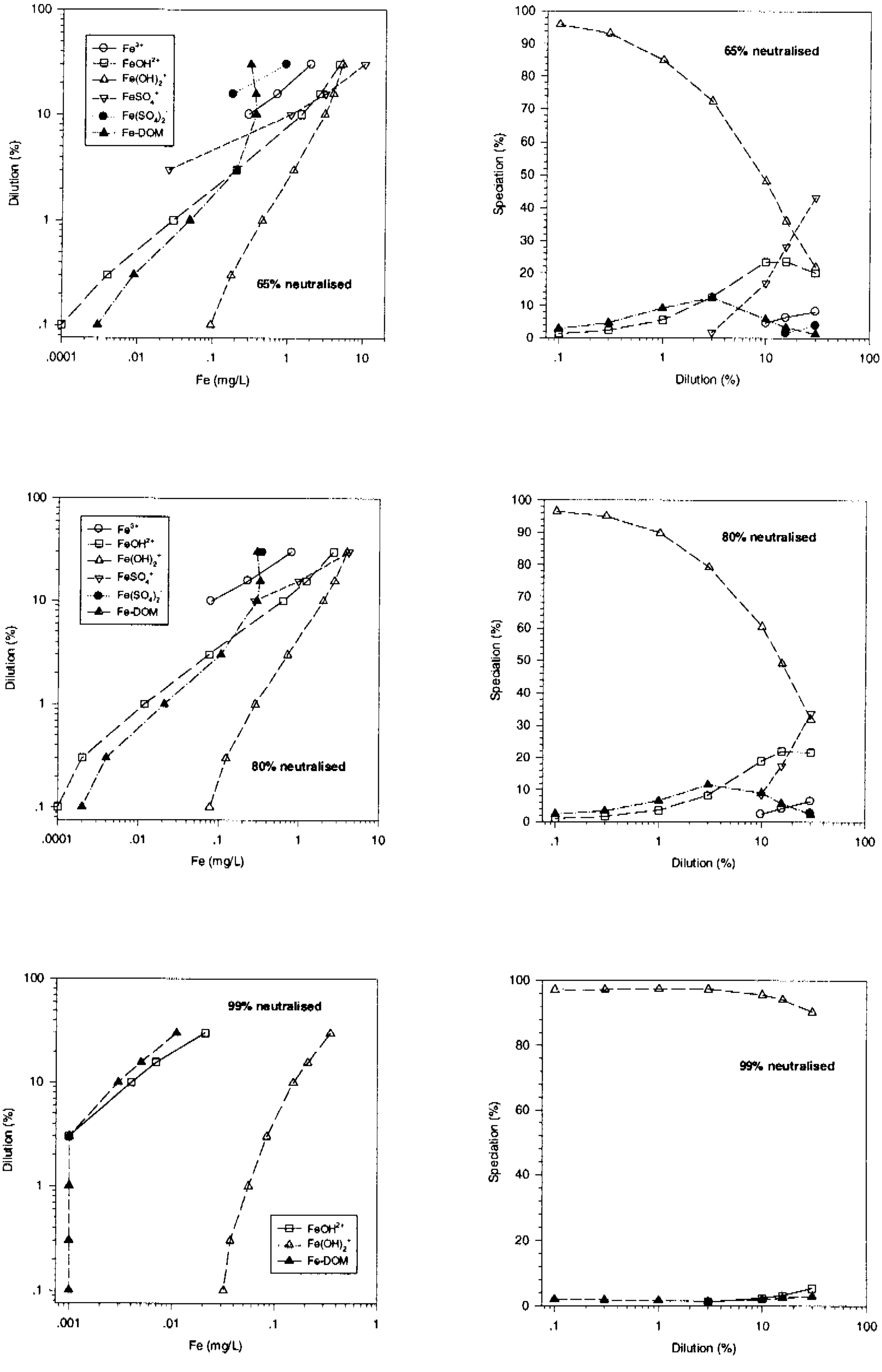


Figure 5.23 The effects of a neutralisation endpoint of pH 6.5, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L Fe) (left) and proportion (right) of soluble Fe (III) species in the Queen and King Rivers (power station off)

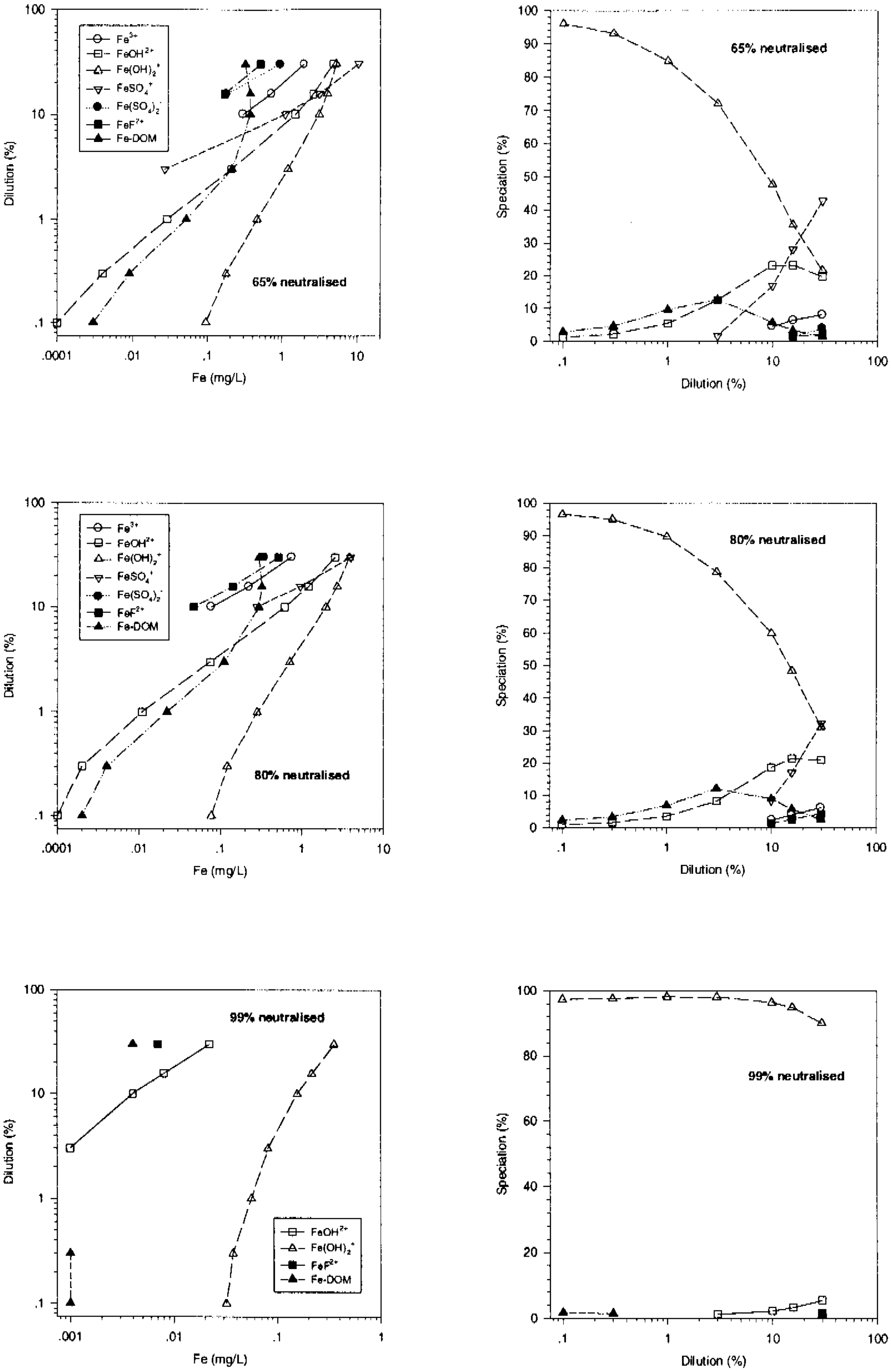


Figure 5.24 The effects of a neutralisation endpoint of pH 6.5, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L Fe) (left) and proportion (right) of soluble Fe (III) species in the Queen and King Rivers (power station off)

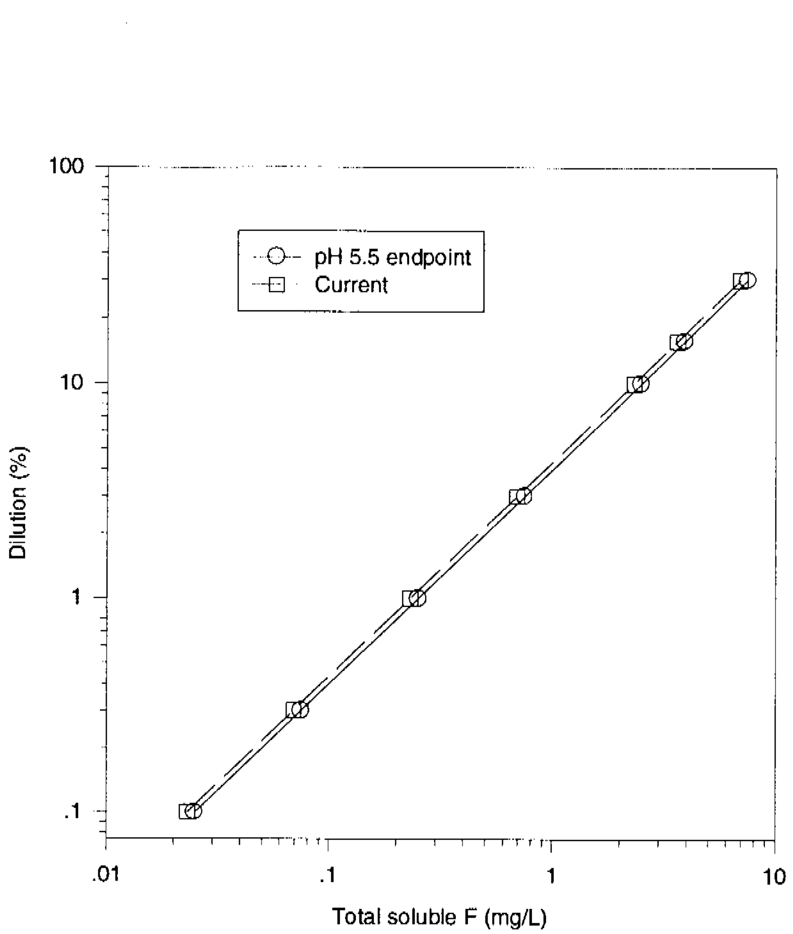
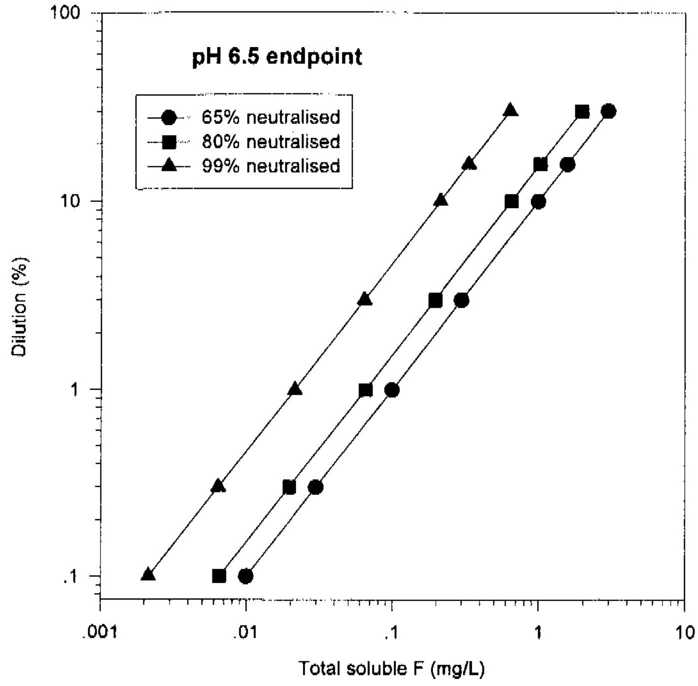


Figure 5.25 Predicted total soluble F (mg/L) in the Queen and King Rivers (power station off) from variable dilution under current conditions and neutralisation of acid drainage to pH 5.5

Table 5.12 Dissolved F species (% of total soluble F) in the King River under median flow with power station on as influenced by SX/EW and the percentage of acid drainage neutralised

	No SX/EW							**SX/EW**		
	% neutralised to pH 6.5				**% neutralised to pH 5.5**					
Species	**Current**	**65**	**80**	**99**	**65**	**80**	**99**	**65**	**80**	**99**
AlF^{2+}	97.3	92.1	84.7	38.0	88.3	75.9	36.2	88.1	75.4	35.5
AlF_2^+	–	1.2	1.5	–	3.5	6.4	9.4	3.5	6.5	9.3
$AlF_{3\,(aq)}$	–	–	–	–	–	–	1.9	–	–	1.9
F^-	1.8	6.6	13.6	60.6	8.0	17.1	52.2	8.1	17.5	52.9

The speciation of fluoride, and particularly the predominance of the F^- ion under low ionic strength conditions, is very sensitive to pH. To demonstrate this point consider the dilution of a median flow of 225 L/s acid drainage which equates to around a 0.3% dilution in the King with the power station releasing at 80000 L/s. Reference to fig 5.28, based on the scenario of power station off, predicts that around 20% of total soluble F is present as the fluoride ion assuming 99% neutralisation of acid drainage and a dilution of 0.3%. Yet for the scenario of power station on and for the same dilution, proportion of acid drainage neutralised and pH endpoint, around 61% of total soluble F is predicted to be present as F^-. The reason for the apparent disparity lies with pH (fig 5.2 & table 5.1). Whereas pH approaches 5.5 in the King for dilute conditions and power station off, with power station on the pH increases to around pH 5.9.



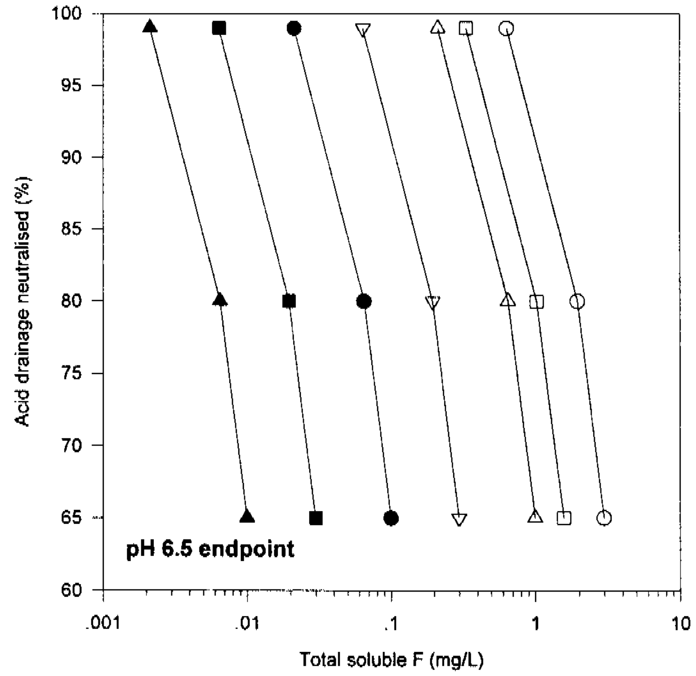
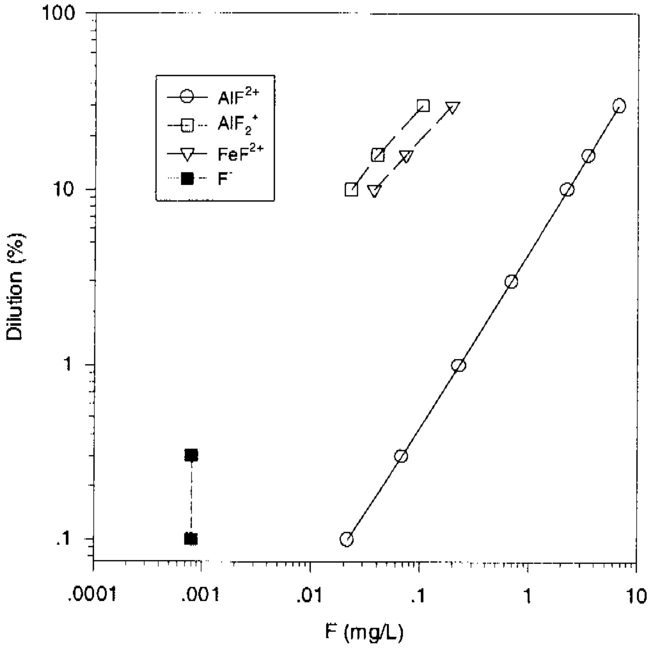


Figure 5.26 Predicted total soluble F (mg/L) in the Queen and King Rivers (power station off) from variable dilution (top) and proportions (bottom) of acid drainage neutralised to pH 6.5

Note: Treatments shown in fig 5.21 (bottom) are from left to right dilutions of mine drainage to 0.1, 0.3, 1, 3, 10, 15.7 and 30%



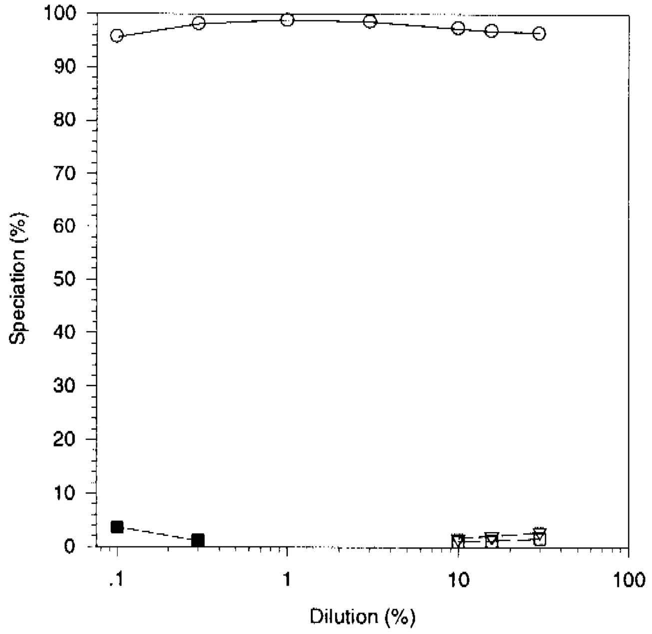


Figure 5.27 Predicted concentration (mg/L F) (top) and the proportion of dominant soluble F species (bottom) in the Queen and King Rivers (power station off) resulting from variable dilution under current conditions

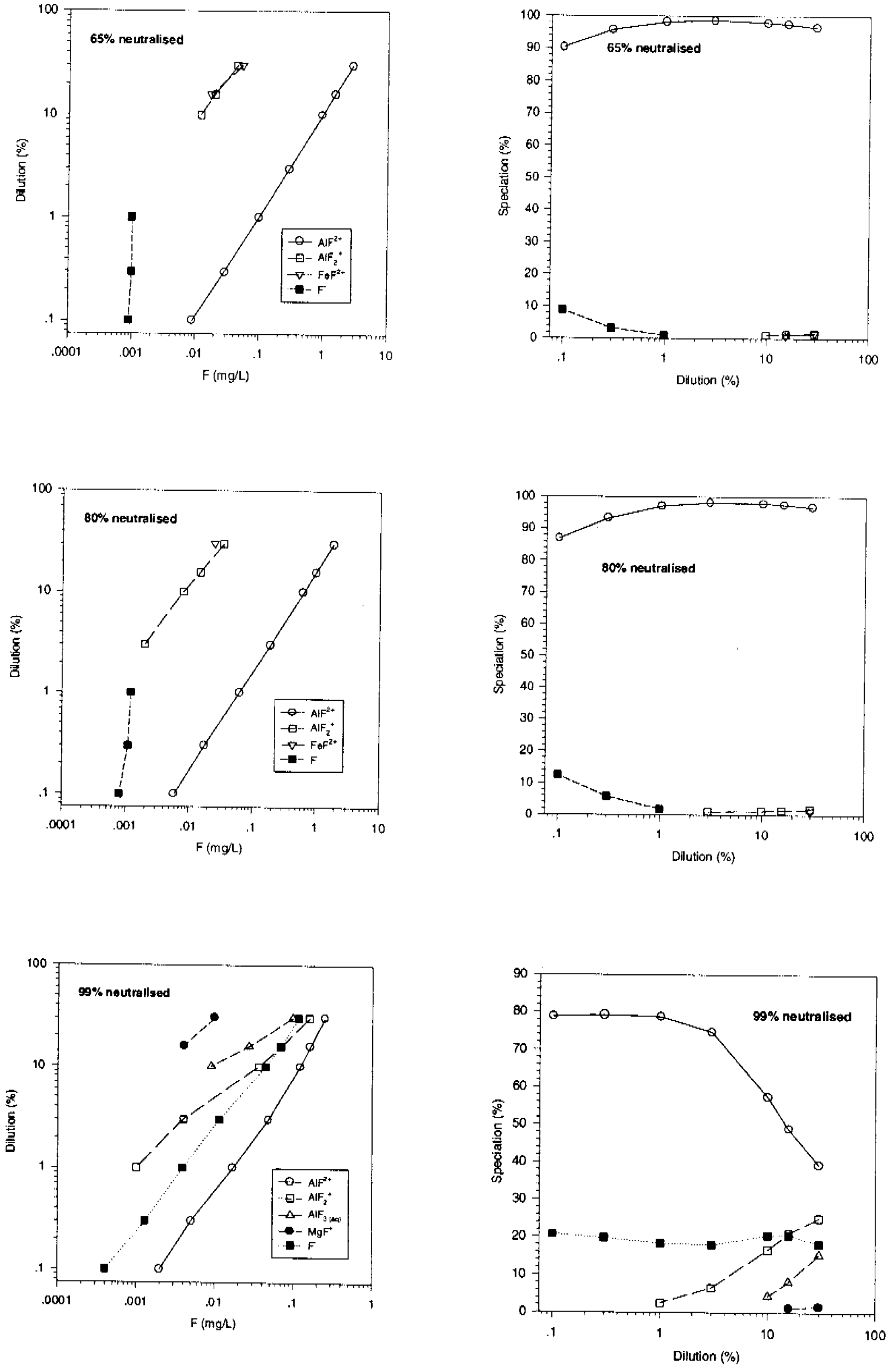


Figure 5.28 The effects of a neutralisation endpoint of pH 6.5, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L F) (left) and proportion (right) of soluble F species in the Queen and King Rivers (power station off)

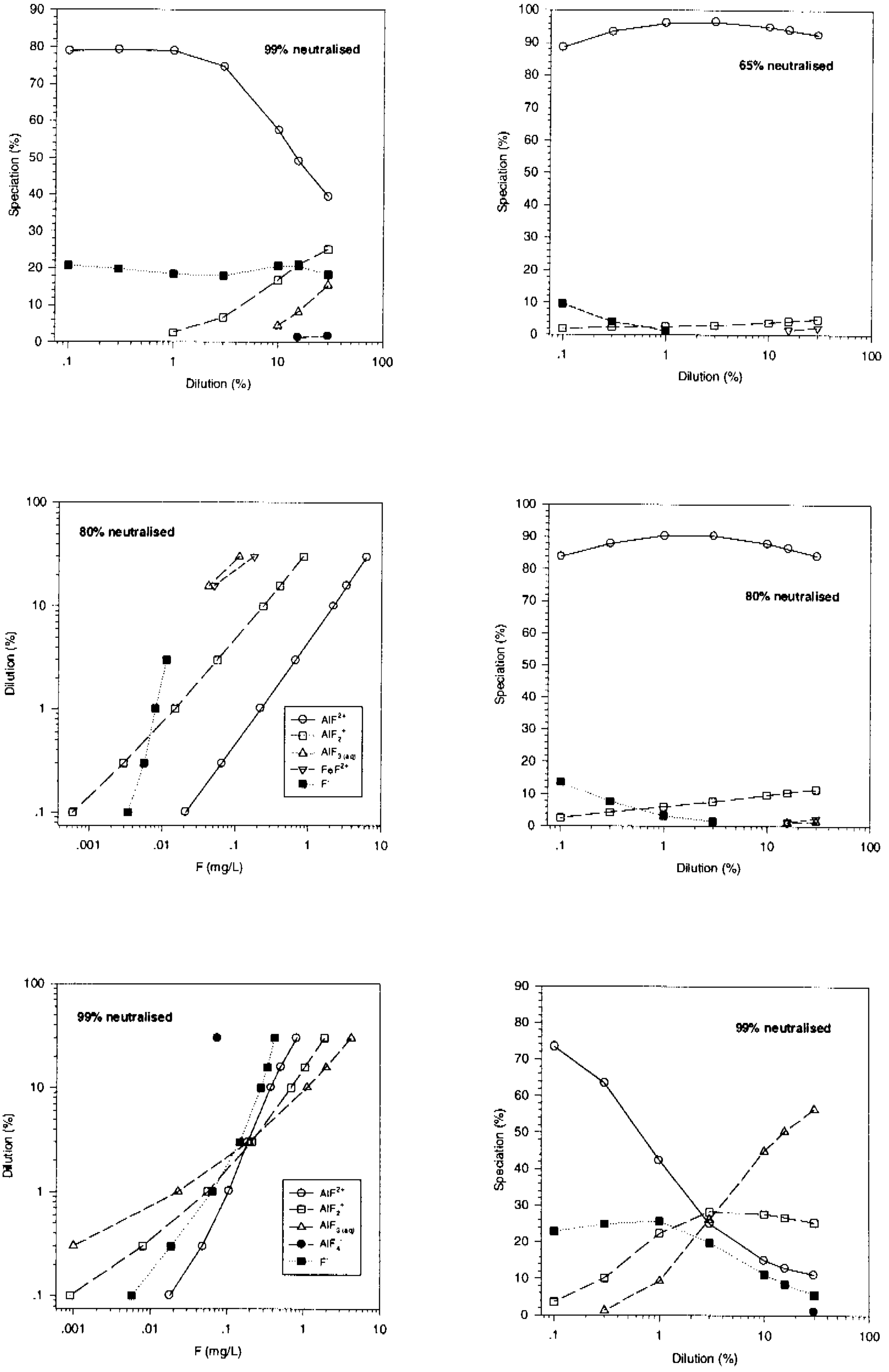


Figure 5.29 The effects of a neutralisation endpoint of pH 5.5, proportion of acid drainage neutralised and variable dilution on the concentration (mg/L F) (left) and proportion (right) of soluble F species in the Queen and King Rivers (power station off)

6 Implications of model predictions

6.1 Introduction

The broad objective of this section is to examine the relationship between remediation of the Queen and King Rivers, by countering influent acid drainage, and biological recovery in so far as recovery is influenced by the chemistry of the river systems. This is important not least for setting water quality objectives, which provide the scope by which biological recovery takes place, but in providing the mechanism by which strategic and operational planning to meet these water quality objectives can be made now and into the future.

In essence, the interpretation of the predicted outcomes from speciation modelling of the scenarios in terms of their implications to potential biological recovery depend critically on three factors: the scenarios used in the model and the constraints they entail; the definition of limits for river water quality parameters; and the interpretations which are made of these parameters against water quality guidelines and/or objectives. The first is dealt with by establishing concentration boundary values within the King and Queen Rivers under a variety of conditions and by discussing the limitations of the data involved, the second by reference to national guidelines on water quality parameters, and the third by taking account of biological response in relation to the lability and/or bioavailability of key chemical indicators. Collectively, these outcomes are then appraised in the light of their implications to biological recovery. Finally, the relationship between remediation strategy and the extent of biological recovery which might be expected is discussed and conclusions drawn.

6.2 Boundary values of key chemical indicators

6.2.1 Concentration gradients

The simplest way of viewing the impact of mine effluent on the Queen and King Rivers is as a set of concentration gradients for each contaminant with the greatest potential limitation to biological recovery shown at the confluence of Haulage Creek with the Queen River, and the least upstream of the King River delta. Irrespective of the degree of remediation which takes place, this scenario is likely to remain true. Since the concentrations of certain contaminants have been shown to be dependent upon the remediation option (see section 5) and given that individual contaminants will vary in their relative toxicities, the potential for biological recovery within the Queen and King River reaches will be defined spatially at points of tolerance for the species concerned.

In this manner and with reference to table 3.1, changes in dilution of mine effluent, assuming constancy in ratio between the flow rates of incoming waters, can be mapped and boundary values set for each river system (table 6.1).

6.2.2 Interpretation of concentration ranges of total soluble contaminants

As a first pass, the ranges for total soluble concentrations contained in table 6.1 were compared with the current Australian national water quality guidelines (ANZECC 1992) (table 6.2) which are based on total dissolved concentrations in unfiltered samples acidified to <pH 2. For Cu, the ambient concentration in unimpacted waters equals the ANZECC guideline of 5 ppb and in the case of Al exceeds the ANZECC value by between 4–15 fold (table 2.4). Consequently, under all the modelled scenarios (and all dilutions) involving the mixing of mine drainage with river water, ANZECC water quality guidelines for Cu and Al are surpassed. The iron (III) guideline is exceeded in the Queen and King Rivers when ≤80% of acid drainage is neutralised to either pH 5.5 or 6.5 and the power station is off. Total soluble zinc in the Queen and King Rivers irrespective of the proportion of acid drainage

neutralised to pH 6.5 or 5.5 is always higher than the guideline value except when the power station operates. In the absence of ANZECC recommendations for F and Mn, alternative sources of data on their toxicities to freshwater ecosystems are clearly required. To conclude, therefore, a first inspection of the model predictions indicates that the principle limiting chemical factors to biological recovery within the Queen and King Rivers are likely to be Cu and Al.

6.3 Bioavailability and toxicity

6.3.1 Cu

Boundary limits for $Cu^{2+}_{(aq)}$ *concentration in the Queen and King Rivers*

The principal form of biologically available Cu in well-oxidised freshwater systems is the cupric ion, $Cu^{2+}_{(aq)}$ (Deighton & Goodman 1995) which effectively determines toxicological response. It has been suggested that hydroxy-Cu complexes might also be toxic to aquatic life (Shaw & Brown 1974; Chakoumakos et al 1979) but, practically, this is impossible to verify because pH and hydroxy-Cu concentration cannot be changed independently of each other in toxicity tests (Borgmann 1983).

Speciation modelling predicts that within the Queen River and the upper reach of the lower King with the power station inactive (ie assuming about 10% dilution), the free cupric ion accounts for around 80% of total soluble Cu (fig 5.11) irrespective of the proportion of acid drainage neutralised or its endpoint. Downstream from the confluence of the King and Queen, dilution favours a disproportional decrease in Cu^{2+} activity because increasingly a greater proportion of total soluble Cu becomes complexed with dissolved organic matter (fig 5.11). With high dilution resulting from the operation of the power station, between 30–60% of total soluble Cu, depending on the treatment of acid drainage, is present as $Cu^{2+}_{(aq)}$ (table 5.4). Using the same boundary limits for dilution as before (table 6.1), predicted concentration ranges for $Cu^{2+}_{(aq)}$ are given in table 6.3.

Water quality guidelines

Reference to table 6.3 indicates that the only condition which results in a concentration of bioavailable Cu that is less than the ANZECC guideline (table 6.2) is when 99% of acid drainage is neutralised to pH 6.5 and that this solely relates to the lowest reaches of King River with the power station on (ie around 0.3% dilution).

In keeping with dilution rates, predicted $Cu^{2+}_{(aq)}$ concentration varies by about twofold in the Queen and in the King by between three to fourfold with the power station off. The difference between maximum and minimum $Cu^{2+}_{(aq)}$ concentrations on a 24 h cycle in the King (assuming a 12 h power station operating period) extends to around 60–70 fold. Consequently, given the wide concentration range and its diurnal change in the King, the most ideal and appropriate procedure in this case from which to derive a guideline would be a 12 h acute toxicity test coupled with a measure of longer term effects (ie chronic toxicity). Table 6.4 summarises some findings from a review of the literature undertaken by MacDonald (1994) in the context of the Fraser River, Canada. Table 6.4 is also augmented with data from CCREM (1987) and recently published South African water quality guidelines (Roux et al 1996).

Water hardness as a factor influencing Cu toxicity

The toxicity of Cu is reduced in the presence of Ca and Mg due to inter-ion competition of sorption and carrier sites during biological uptake (Miller & Mackay 1980; Winner 1985). For example, taking hardnesses of 50, 100 and 200 mg equiv. $CaCO_3$/L the USEPA (1986) calculate critical 4-day average concentrations of Cu to be 6.5, 12 and 21 µg/L. In the Queen and King

Rivers, water hardness would span this range with progressive dilution downstream of neutralised acid drainage (table 6.5). There is therefore some scope for hardness mitigating the effects of Cu toxicity in the dilution range of 3–10% in the King but, in accordance with the modelled scenarios, only when almost all (ie 99%) of the acid drainage is neutralised to pH 6.5.

Differences in composition of mine waters

For simplicity, the development of scenarios for modelling has taken the composition of the combined waters of Conveyor and North Lyell Tunnels as representative of acid drainage from Haulage Creek so that a worst-case in terms of Cu load has been described. However, if 80% of acid drainage was to be neutralised (assuming on the basis of Cu loads to represent Conveyor and West Lyell Tunnell sources) then the remaining 20% of raw acid drainage (by Cu load) would have a composition determined by the remaining sources of which the West Lyell waste rock dumps are the most important. The median concentration of total soluble Cu in Haulage Creek above the Tunnels is 82 mg/L (table 2.5) which implies that on the basis of dilution and the conservativism of Cu (see section 5.2), predicted total soluble Cu would be 79% of the values given in table 5.2 and figs 5.5–5.7. Speciation modelling reveals that $Cu^{2+}_{(aq)}$ would be reduced by around 14% compared with the data given in table 6.3 assuming neutralisation of ≥80% acid drainage to pH 6.5. Hence taking account of a lower Cu concentration in mine waters from sources other than the Tunnels does not much alter the constraints imposed on biological recovery by virtue of the toxicity of the predicted concentration of $Cu^{2+}_{(aq)}$. However, while a lower Cu concentration may bring marginal benefits to the King River, the flip side is that the median concentrations of Fe and Al (based on Fe ratios in the absence of data) are estimated to be around three times higher in drainage from waste rock which has a lower pH compared with Tunnel water. In turn, this will increase the pH buffering of acid drainage and possibly exacerbate Al toxicity and mean that the lime requirement to pH 6.5 is about three times higher. Importantly, the higher Al content of drainage from waste rock implies an underestimation of the total soluble Al load entering the Queen River according to the model scenarios.

Dissolved organic matter as a complexer of Cu

Dissolved organic matter plays an important role in complexing copper in natural (Anderson et al 1990) and mine-impacted (Apte et al 1995) riverine, and estuarine (Apte et al 1990a) environments. Given that Cu is exceedingly more toxic to aquatic life compared to intake of water by mammals (Vymazal 1995), its complexation with DOM is a crucial part of speciation modelling because DOM reduces the bioavailability and potential toxicity of total dissolved Cu (Winner 1985; Meador 1991). In river and estuarine systems it has been shown that it is not unusual for as much as 99% of naturally-occurring, dissolved total Cu to be complexed with DOM (Apte et al 1990a) and that the Cu complexing capacity (CuCC) of DOM can be in excess of 12.7 µg/L (ie 200 nM) (Apte et al 1990b). In Gordon River water, Carpenter et al (1991) found CuCC to be 7.9 µg/L compared with 1.0–4.3 µg/L in Macquarie Harbour. However, recent estimates by Teasdale et al (1996) of the CuCC of Macquarie Harbour waters indicate that CuCC is around 31 µg/L, much higher than that estimated by Carpenter et al (1991).

Table 6.1 Summary of boundary values for dilution of raw + neutralised acid drainage, pH and concentrations of total soluble contaminants (mg/L) in the Queen and King Rivers under various scenarios

			Queen River		King River			
					Power station off		Power station on	
pH endpoint	**AD neutralised (%)**	**Parameter**	**Max. dilution**	**Min dilution**	**Max dilution**	**Min dilution**	**Max dilution**	**Min dilution**
		Dilution (%)	15.7	>30	3.0	10.7	0.26	0.27
6.5 and 5.5	65	pH	3.41	<3.30	3.92	3.52	5.00	
	80		3.57	<3.43	4.13	3.71	5.20	
	99		4.69	<4.49	5.07	4.83	5.91	
6.5 (5.5)	65	Total soluble Cu (mg/L)	5.83 (8.96)	>11.1 (17.1)	1.12 (1.72)	3.72 (5.71)	0.091 (0.137)	
	80		3.42 (7.26)	>6.53 (13.9)	0.658 (1.39)	2.18 (4.63)	0.055 (0.112)	
	99		0.366 (5.12)	>0.694 (9.78)	0.074 (0.982)	0.235 (3.26)	0.010 (0.080)	
5.5 + SX/EW	65		7.23	>13.82	1.39	4.61	0.111	
	80		5.14	>9.83	0.987	3.28	0.080	
	99		2.50	>4.77	0.481	1.59	0.042	
6.5 (5.5)	65	Total soluble Al (mg/L)	8.70 (10.08)	>16.6 (19.20)	1.72 (1.99)	5.57 (6.45)	0.150 (0.170)	
	80		5.00 (6.70)	>9.49 (12.7)	1.02 (1.34)	3.21 (4.30)	0.096 (0.121)	
	99		0.321 (2.43)	>0.545 (4.57)	0.122 (0.524)	0.232 (1.57)	0.027 (0.058)	
6.5 and 5.5	65, 80 and 99	Total soluble Mn (mg/L)	17.6	>33.6	3.37	11.21	0.268	
6.5 and 5.5	65, 80 and 99	Total soluble Zn (mg/L)	1.88	>3.60	0.36	1.20	0.028	
6.5 and 5.5	65	Total soluble Fe (mg/L)	11.2	>24.4	1.65	6.47	0.133	
	80		5.65	>12.4	0.917	3.32	0.076	
	99		0.224	>0.386	0.086	0.159	0.012	
6.5 (5.5)	65	Total soluble F (mg/L)	1.57 (3.92)	>3.00 (7.50)	0.300 (0.750)	0.999 (2.50)	0.023 (0.058)	
	80		1.02 (3.92)	>1.96 (7.50)	0.196 (0.750)	0.653 (2.50)	0.015 (0.058)	
	99		0.336 (3.92)	>0.642 (7.50)	0.064 (0.750)	0.214 (2.50)	0.005 (0.058)	

Table 6.2 ANZECC water quality guidelines for the protection of freshwater aquatic ecosystems

Total concentration (µg/L)					
Al	**Cu**	**F**	**Fe (III)**	**Mn**	**Zn**
<5	2–5	not given	1000	not given	5–50

Table 6.3 Boundary concentrations of $Cu^{2+}_{(aq)}$ (mg/L) in the Queen and King Rivers under maximum and minimum dilution and various scenarios

		Queen River		King River		
				Power station off		Power station on
pH endpoint	**AD neutralised**	**Max**	**Min**	**Max**	**Min**	**Max**
6.5	65%	4.78	>8.56	1.01	3.17	0.054
	80%	2.81	>5.06	0.570	1.86	0.026
	99%	0.269	>0.514	0.044	0.168	0.003
5.5	65%	7.33	>13.1	1.54	4.85	0.080
	80%	5.95	>10.7	1.20	3.93	0.054
	99%	4.06	>7.48	0.728	2.61	0.010
5.5+SX/EW	65%	5.91	>10.6	1.24	3.92	0.064
	80%	4.21	>7.59	0.845	2.78	0.038
	99%	1.94	>3.62	0.325	1.23	0.013

In the MINTEQA2 speciation model, there are three DOM linked variables which determine the quantity of Cu which is complexed per unit mass of DOM. These are the concentration of dissolved organic carbon, the charge density of the organics and the stability constant for Cu complexation. There are no data for the CuCC of King River water and since the derivation of any stability constant describing the reaction of Cu with DOM is dependent upon the conditions under which it is made, such as pH, ionic strength and the activities in solution of competing ions, an extrapolation cannot be made from the data given above. In this study, we assumed the same charge density of 1 mol/kg (equivalent to 1×10^{-6} mol/mg C) as used previously by EGI in their speciation modelling (MLMRC 1995a) but this probably overestimates the charge density of DOM. For example if a CuCC of 30 µg/L is taken (cf Teasdale et al 1996; table 4.4, p 38) to represent surface water in Macquarie Harbour and assuming a DOM of 5 mg/L C (cf Teasdale et al 1996; table 4.1, p 32), this equates to a proton charge density on DOM of approximately 0.2 mol/kg. To repeat, however, care has to be exercised in extrapolating results from one chemical environment to another since the charge density of DOM and its configuration (Schnitzer 1991) will change in response to pH and ionic strength.

As a counter to the probable over-estimation of charge density of DOM, it is likely that there was under-estimation of the *mean* stability constant of the Cu-DOM complex. In our model, we assumed unidentate metal to ligand stoichiometry and used default values supplied by MINTEQA2 Version 3.11 for metal-DOM stability constants whose log K (±1.7) were as follows: Mg^{2+} 1.9, Ca^{2+} 2.9, Zn^{2+} 3.5, H^{+} 3.87, Cu^{2+} 4.9, Al^{3+} 5.2 and Fe^{3+} 7.7. This order is in broad agreement with IR spectra of carboxylate binding (Juste & Delas 1966) except for $Cu^{2+} > Al^{3+}$, fluorescence quenching studies (Ryan & Webber 1982) and the strength of binding of metals to humic substances between pH 4–6 (Kerndorff & Schnitzer 1980).

While 1:1 complexes commonly form, changes in metal, DOM and H^+ concentrations may influence stoichiometry (Schnitzer & Skinner 1963). In the case of Cu^{2+}, strong inner-sphere complexes occur particularly at low metal to DOM ratios (Senesi 1992) which are typified by conditional stability constants of the order of 10^8–10^{14} (Apte et al 1990b). The trivalent cations, Fe^{3+} and Al^{3+}, compete with Cu^{2+} for these strong binding sites (Cressey et al 1983). As metal : DOM ratios are increased, there is a greater propensity for weak binding of Cu^{2+} because outer-sphere complexes form with a concomitant increase of liklihood of exchange with other competing metal species.

Although the occurrence of highly stable binding of Cu by DOM is implied under dilute *equilibrium* conditions in the King River, there is evidence from other studies (Apte et al 1995) that *psuedo-equilibrium* may be attained by Cu as a consequence of kinetic considerations of its complexation by DOM. In this way, there is a tendency for relatively weak Cu-DOM complexes to form initially over a time-frame of hours followed by slower equilibration from the migration of sorbed Cu to strong sites over days. Consequently, the relative magnitude of the Cu stability constant used in this study for speciation modelling, given the relatively short transit time for waters to flow from source to Macquarie Harbour, is likely to be of the correct magnitude. The results of Apte et al (1995) also imply that given the long residence time of waters in Macquarie Harbour, strong complexes of Cu with DOM are kinetically favoured.

In summary, the predictions for Cu-DOM complexation are probably as precise as they can be given the limited data available. An obvious shortfall in information is the CuCC of King River water and any further work to tune the model to improve the prediction of $Cu^{2+}_{(aq)}$ in the King would benefit from this data.

Adsorption of Cu to suspended solids

The role of suspended solids in providing a surface for Cu adsorption in the context of this study is not known. However, the most important surface to which Cu might be adsorbed is ferrihydrite since this mineral is a precipitation product from the mixing of raw acid mine drainage with its neutralised counterpart and river water. The concentration of natural suspended solids in Lake Burbury water, the principal source of the King River, is exceedingly low (commonly <5 ntu and typically 1–2 ntu; A Sanger pers comm), and are therefore unlikely to influence the solution phase chemistry of Cu to any marked degree.

The cupric ion is adsorbed rapidly on a variety of hydrous metal oxides (Kinniburgh & Jackson 1981) with its adsorption edge determined by its pK_1 value (ie dissociation of the metal to give the $CuOH^+$ hydrolysis product) and the point of zero charge (PZC) for the solid surface (Barrow 1985). The concentration of ferrihydrite has a PZC of approximately 7.9 (0.0015 M $NaNO_3$) and shows 50% sorption of Cu^{2+} from solution at around pH 5.5 (10^{-3} M Fe; 10^{-6} mol/L Cu; $I = 10^{-1}$ mol/L) (Davis & Leckie 1978). Under these latter conditions, this equated to the sorption of 0.03 and 1.3 µg Cu/mg Fe (as ferrihydrite) at pH 5 and 6 respectively. In a study of the Carnon River, Johnson (1986) found a surface density of around 1.18×10^{-2} mol Cu per mol Fe associated with Fe oxyhydroxides in a river system contaminated with mine drainage. Particulate Fe in waters downstream from mine influent ranged from 2.7–26.0 mg/L (mean = 12.6 mg Fe/L) in contact with an average dissolved Cu concentration of 0.6 mg/L. At pH 4, the ratio of bound:dissolved Cu ranged between 1–10% and at pH 5, between 10–50%.

Table 6.4 Guideline values for total Cu (µg/L) to protect freshwater aquatic ecosystems

Conc. (µg/L)	Comments	Reference
0.05*LC_{50}	Australia; recommendation	Hart (1974)
0.5	Proposed guideline for Ontario; hardness > 20 mg $CaCO_3$/L	Environment Ontario (1989)[1]
0.53	South Africa; chronic toxicity; <60 mg $CaCO_3$/L	Roux et al (1996)
1	Proposed guideline for Ontario; derived by TTA[2]	OMEE (1994)[1]
1.3	Netherlands; derived by TTA[2]	Stortelder et al (1989)[1]
1.5	South Africa; chronic toxicity; 60–119 mg $CaCO_3$/L	Roux et al (1996)
1.53	Quebec; chronic toxicity; derived by TTA[2]	MENVIQ (1990)[1]
1.6	South Africa; acute toxicity;<60 mg $CaCO_3$/L	Roux et al (1996)
<2	British Columbia; 30-day average; ≤50 mg $CaCO_3$/L	Pommen (1989)[1]
2	British Columbia; 30-day average; ≤50 mg $CaCO_3$/L; TTA[2]	BCMOELP (1994)[1]
2	Quebec; chronic toxicity; derived by TTA[2]	MENVIQ (1990)[1]
2.4	South Africa; chronic toxicity; 120–180 mg $CaCO_3$/L	Roux et al (1996)
2.65	Quebec; chronic toxicity	MENVIQ (1990)[1]
2.8	South Africa; chronic toxicity; >180 mg $CaCO_3$/L	Roux et al (1996)
1–3	Netherlands; national guideline	MHSPE (1994)
3.1	Netherlands; derived by TTA[2]	Stortelder et al (1989)[1]
3.91	Quebec; chronic toxicity; derived by TTA[2]	MENVIQ (1990)[1]
4	British Columbia; >35 mg $CaCO_3$/L	Swain & Holms (1985)[1]
2–4	Canadian national guideline; TTA[2]; depends on hardness	CCREM (1987)
4.6	South Africa; acute toxicity; 60–119 mg $CaCO_3$/L	Roux et al (1996)
5	Quebec; provincial guideline; derived by TTA[2]	OMEE (1994)[1]
5.16	Great Lakes; chronic toxicity; derived by TTA[2]	USEPA (1992)[1]
3–6	British Columbia; depends on hardness	Swain & Holms (1985)[1]
7.3	Great Lakes; max. concentration criterion; derived by TTA[2]	USEPA (1992)[1]
7.5	South Africa; acute toxicity; 120–180 mg $CaCO_3$/L	Roux et al (1996)
10	Saskatchewan	SDEPS (1988)[1]
10.95	Quebec; acute toxicity; derived by TTA[2]	MENVIQ (1990)[1]
12	South Africa; acute toxicity; >180 mg $CaCO_3$/L	Roux et al (1996)
12	USA; chronic toxicity; >100 mg $CaCO_3$/L	USEPA (1986, 1990, 1993)[1]
14.57	Great Lakes; acute toxicity; derived by TTA[2]	USEPA (1992)[1]
18	USA; acute toxicity; >100 mg $CaCO_3$/L	USEPA (1986, 1990; 1993)[1]
20	Alberta; max. concentration	Alberta Environment (1977)
21.1	Quebec; acute toxicity; derived by TTA[2]	MENVIQ (1990)[1]
28.3	Quebec; acute toxicity; derived by TTA[2]	MENVIQ (1990)[1]
40	Europe; salmonid & cypinid waters; 100 mg $CaCO_3$/L	CEC (1978)

1 cited by MacDonald (1994)

2 theoretical toxicological approach

Table 6.5 Range in water hardness in the Queen and King Rivers (mg equiv. $CaCO_3$/L) as a function of dilution of neutralised acid drainage

	Acid drainage neutralised (%)		
Mine drainage (% by vol)	**65**	**80**	**99**
30	490	510	536
15.7	272	283	297
10	182	190	199
3	63	66	69
1	26	27	28
0.3	13	13	13
0.1	9	9	9

In the present study, the importance of ferrihydrite as an adsorbing phase has been examined in the light of boundary pH values and the fact that as progressively more acid drainage is neutralised, the yield of ferrihydrite as a precipitate within the rivers declines (ie it is removed following neutralisation of acid drainage). Boundary pH values are given in table 6.6, and table 6.7 provides the predicted yield of ferrihydrite per unit volume.

There are several factors which question the importance of ferrihydrite in controlling Cu concentration in the Queen and King Rivers. Firstly, the concentration of ferrihydrite in the King River (table 6.7), on the assumption that it remains in suspension, is low (ie <3.1 mg Fe/L). As progressively more acid drainage is neutralised, the concentration of ferrihydrite will fall to <0.14 mg Fe/L when 99% of acid drainage is treated (table 6.7). Allied with this, low suspended solids concentration is a pH ranging between 4 to 5 (table 6.6). According to Davis and Leckie (1978), <20% of total soluble Cu was adsorbed on to Fe oxyhydroxides at <pH 5. Secondly, in natural environments, the surface of iron and other oxy-hydroxides become modified by coatings of organic matter (Tipping 1981; Gu et al 1994) which may reduce the capacities of the oxy-hydroxides to bind metals. Thirdly, whilst we have assumed that true equilibrium of Fe^{3+} has been attained (from the total oxidation of reduced forms and its precipitation as ferrihydrite), under cold, acid conditions the kinetics of abiotic oxidation are slow (Hem 1989) which may therefore mean that the yield of ferrihydrite has been overestimated.

Table 6.6 Boundary pH values in the Queen and King Rivers under maximum and minimum dilution and various scenarios

		Queen River		King River		
				Power station off		Power station on
pH endpoint	**AD neutralised**	**Max**	**Min**	**Max**	**Min**	**Max**
6.5 & 5.5	65%	3.41	<3.30	3.92	3.52	5.00
	80%	3.57	<3.43	4.13	3.71	5.20
	99%	4.69	<4.49	5.07	4.83	5.91

Further work is required to validate the kinetics of ferrihydrite precipitation in the Queen and King Rivers and to verify whether Cu sorption to Fe oxyhydroxides is an important process modifying Cu bioavailability in these river system under the modelled scenarios. In the absence of a sorption component to the model, prediction of $Cu^{2+}_{(aq)}$ concentration is likely to be conservative.

Summary

- There appears to be little scope for expecting long-term recovery of the rivers based upon the predicted bioavailability and toxicity of Cu unless almost all (≥99%) of the acid drainage currently entering Haulage Creek is neutralised to at least pH 6.5.
- The use of SX/EW in conjunction with neutralisation of acid drainage to pH 5.5 confers less advantage in terms of potential Cu toxicity to aquatic life compared with neutralisation to pH 6.5. Hence, if SX/EW is to proceed, liming of the raffinate to pH 6.5 is recommended.
- Further data is required on the copper complexing capacity of dissolved organic matter in King River water.
- The importance of suspended matter in modifying the bioavailability of Cu under the modelled scenarios requires to be elucidated.

6.3.2 Aluminium

The toxicity of Al

Bioavailable aluminium is poorly defined in the literature, has proved difficult to set in terms of water quality guidelines and has been and continues to be subject to contradictory interpretation some of which has arisen from a failure to adequately relate speciation and toxicological response to chemical composition. The cause of much of this problem appears to centre around the relative complexity of the chemistry of Al speciation in which a variety of hydrolysis products of monomeric and polymeric character can complex with anions, principally as sulphato- and fluoro- complexes. Hence, in toxicological response studies it has proved difficult to diagnose the relative toxicity of Al species, often requiring an understanding of the physiological and biochemical response mechanisms of the organism to Al stress and its relationship to Al form.

Table 6.7 Concentration (mg/L Fe) of ferrihydrite precipitate in the Queen and King Rivers under maximum and minimum dilution and various scenarios

		Queen River		King River		
				Power station off		Power station on
pH endpoint	AD neutralised	Max	Min	Max	Min	Max
6.5	65%	3.84	>4.40	1.26	3.14	NP[1]
	80%	2.97	>4.02	2.18	0.76	NP
	99%	0.23	>0.46	0.03	0.14	NP
5.5	65%	3.80	>4.31	1.24	3.11	NP
	80%	2.95	>3.97	2.17	0.76	NP
	99%	0.23	>0.46	0.03	0.14	NP

[1] NP – Not present

Because of the confusion which surrounds the toxicity of Al, a variety of interpretations of Al toxicity have arisen which have been reviewed by Kinraide and Parker (1989). For example, the latter are unconvinced of the hypothesis that mononuclear hydroxy-Al forms (ie $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$) to the exclusion of others are the main forms of Al toxicity to organisms (Driscoll et al 1980; Petersson et al 1985; Alva et al 1986). Rather, they ascribe the effect of pH increase which can give rise to an increase in toxicity at constant total soluble Al to the formation of the polymeric cation $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. This polynuclear form of Al co-exists with monomeric Al and has a toxicity at least an order of magnitude greater than Al^{3+} (Kinraide & Parker 1989) but its formation is dependent on the activity ratio $Al^{3+}/(H^+)^3$ being >8.8. Special account of the possible formation of polymeric Al was not taken in the present study. Whether it would form in the King River would depend on kinetics and the degree of ion saturation required to activate polymerisation. If it did form, then this would most likely occur at relatively high pH when the power station is on. Consequently, given its highly toxic nature, this might cause biological stress over part of the active 12 h power station cycle and further work might be advisable to examine whether polymeric Al is likely to be a limiting factor determining biological recovery under these conditions.

There is evidence to suggest that the formation of fluoro-Al complexes can reduce the potential toxicity of Al to fish (Wilkinson et al 1990) and plants (Cameron et al 1986), although in the case of fish this may only give rise to a marginal reduction in Al binding at the gill compared to the absence of F (Wilkinson et al 1993). Similarly, it has been shown that sulphato- complexes of Al are non-toxic to plants (Cameron et al 1986; Kinraide & Parker 1987). Mechanistic response models using conditional stability constants to describe surface complexation of monomeric Al species on gill surfaces have been developed (Neville & Campbell 1988; Wilkinson et al 1990; Wilkinson et al 1993) and distinction made between adsorbed and absorbed Al in the toxicological response of fish (Parent et al 1988).

Fluoro-Al complexes are dominant forms of Al in impacted and natural waters (Hem 1989). Hence, any amelioration of the toxicity of Al on aquatic organisms by the formation of fluoro- or sulphato-complexes will depend critically on kinetics. pH and temperature are master variables determining the rate of formation of fluoro-Al complexes (Plankey et al 1986; Townsend & Bache 1992; Radic & Bralic 1995). In terms of the conditions which would exist in the Queen and King Rivers under the model scenarios, the relatively low temperature of the river water (taken as 10°C for modelling) would result in a relatively slow rate of formation of fluoro-Al complexes. For example, taking initial concentrations of Al^{3+} and F^- of 0.79 and 0.24 mg/L respectively (pH = 3.85 and I = 0.1M), Plankey et al (1986) found that the half-life period for the formation of AlF^{2+} increased from 16 minutes at 20°C to 125 minutes at 9°C. In addition, the rate of Al-F complexation is at a minimum at pH 3 (Plankey et al 1986; Townsend & Bache 1992) and increases significantly at pH>4.35 (Plankey et al 1986). In this way (C leGras pers comm), at the ambient pH (predicted under the model scenarios) and temperature of the Queen River, the half-life of the complexation reaction is in the order of hours, and negligible complexation will occur during the transit time. Due to the higher pH of the King River, complexation will be much more rapid because of the greater rate of F^- substitution in hydroxyaluminium complexes. At 10°C, and under the concentration range of the diluted reactants with the power station on, the half-life of complexation in the King River would be in the order of minutes, but cannot be evaluated precisely because of the paucity of data on the rate of substitution of F^- in di- and tri-hydroxy aluminium complexes. Most probably, the reaction would be near completion in about 1 hour (C leGras pers comm).

Dissolved organic matter is an important complexer of Al in soil solution (Pohlman & McColl 1988; Kuiters & Mulder 1993) and in natural waters (Burrows 1977; Hem 1989) and thereby reduces the potential toxicity of Al to aquatic organisms. According to Hawke et al (1996), fulvic acid can bind Al more strongly and at a lower pH than Cu, and has a higher Al complexing capacity (AlCC) than CuCC. In unfiltered natural river waters, the AlCC ranged from 0.18–0.26 mg/L, between 0.07 and 0.23 mg/L higher than the ambient total soluble Al concentration (Hawke et al 1996). As demonstrated in figs 5.17 and 5.18, it is predicted that between 5–36% of total soluble Al from raw acid drainage is complexed with DOM in competition with Cu under median flow in the King River.

In conclusion, inconsistencies of approach, technique and interpretation in the measurement of the toxicity of Al to aquatic life has confounded the development of an agreed set of criteria by which to predict the bioavailability of Al from the known chemical properties and composition of waters. The use of the sum of the activities of $\{Al^{3+}\}$, $\{AlOH^{2+}\}$ and $\{Al(OH)_2^{+}\}$ has been shown to relate poorly to toxicity to plants (Parker et al 1988) with the best estimate being gained from Al^{3+} in the absence of the quantification of the activity of polynuclear Al species (Parker et al 1988).

Boundary values for bioavailable Al in the Queen and King Rivers

In the absence of a recognised procedure for indexing the bioavailabilty of Al to aquatic freshwater species, boundary values were set using Al^{3+} (table 6.8). These boundary values are interesting since they demonstrate the importance of fluoro-complexes in modifying the concentration of Al^{3+} in solution when pH 5.5 as opposed to pH 6.5 is used as the neutralisation endpoint for acid drainage. When the former is used, predicted Al^{3+} concentrations are appreciably lower.

Water quality guidelines

Guidelines are summarised for Australia (table 6.2) and elsewhere (table 6.9) with modifications for pH and water hardness. In view of the poor understanding of the relationship of Al speciation to ecotoxicological response by aquatic organisms, they are difficult to interpret in the context of the present study. In the case of the Australian guidelines (table 6.2), a limit of 5 μg/L total Al is difficult to justify since this figure falls below the concentration which would be expected of waters in equilibrium with gibbsite as the controlling mineral phase below pH 6.5. However, if the highest guideline value of 0.1 mg/L is used from table 6.9 to establish a baseline to adjudge the effects of the model scenarios, then conditions for recovery within the King River, assuming the power station to be off, would be $80\% < x \leq 99\%$, where x is the percentage of acid drainage neutralised. It should be noted, however, that hydroxy- and fluoro-Al complexes may also exert a toxic effect on aquatic life and cannot be discounted.

Summary

- There is a high degree of uncertainity about the relative toxicities of Al species to aquatic organisms and consequently it is difficult to relate speciation predictions to likely biological recovery in the Queen and King Rivers under the modelled scenarios.
- Irrespective of any advantage which might be conferred in terms of reducing Al bioavailability in river water by liming to a lower pH than 6.5, Cu is likely to remain the limiting factor to biological recovery and, if it is to be countered, requires that acid drainage is limed to pH 6.5 rather than 5.5.

- It is recommended that further studies be made of the following to improve biological recovery predictions:
  - the toxicity of waters simulating median flow and power station operation in the King River;
  - the toxicity of waters containing acid drainage neutralised to pH 5.5 and simulating dilution in the King River;
  - the aluminium complexing capacity of King River water and the competition of Al with Cu for organic complexation.
- Current Australian water quality guidelines are inadequate in setting water quality objectives for Al in the Queen and King Rivers.

Table 6.8 Boundary concentrations of $Al^{3+}_{(aq)}$ (mg/L) in the Queen and King Rivers under maximum and minimum dilution and various scenarios

		Queen River		King River		
				Power station off		Power station on
pH endpoint	**AD neutralised**	**Max**	**Min**	**Max**	**Min**	**Max**
6.5	65%	3.73	>6.35	0.948	2.59	0.044
	80%	2.07	>3.51	0.517	1.43	0.020
	99%	0.012	>0.013	0.016	0.013	0.002
5.5	65%	2.69	>4.63	0.689	1.86	0.035
	80%	0.904	>1.59	0.233	0.619	0.014
	99%	0.008	>0.012	0.005	0.006	0.002

Table 6.9 Guideline values for Al (μg/L) to protect freshwater aquatic ecosystems

Conc (μg/L)[1]	Comments	Reference
b'ground + 10%	Ontario; pH 5.5–6.5; natural background	Environment Ontario (1988)[2]
1	South Africa; chronic toxicity; 90 mg $CaCO_3$/L	Roux et al (1996)
5–100	Canada national guideline; depends on pH, Ca and DOM	CCREM (1987)
10	South Africa; acute toxicity; 90 mg $CaCO_3$/L	Roux et al (1996)
15	Ontario; pH 4.5–5.5; inorganic monomeric Al; clay-free	Environment Ontario (1988)[2]
50	British Columbia; dissolved; 30-day av. conc.; derived by TTA	BCMOELP (1994)[2]
75	Ontario; pH 6.5–9; clay free	Environment Ontario (1988)[2]
100	British Columbia; dissolved; pH 6.5; derived by TTA	BCMOELP (1994)[2]

[1]Total unless otherwise indicated; [2]cited by MacDonald (1994)

6.3.3 Other potential contaminants

Manganese

According to the USEPA (1986), it is rare for freshwaters to contain more than 1 mg/L Mn and, therefore, when combined with the relatively high tolerance shown by freshwater aquatic species of 1.5 to more than 1000 mg/L (USEPA 1986), Mn toxicity problems are likely to be rare. Neither the Netherlands, Canada nor Australia provide national guidelines on the protection of aquatic systems from Mn. However, British Columbia (BCMOELP 1994; cited by MacDonald 1994) provides a guideline of 100–1000 μg/L total Mn for freshwater and in South Africa (Roux et al 1996) chronic and acute effect values for cold-water adapted species have been set at 180 and 1300 µg/L Mn at a water hardness of 90 mg $CaCO_3$/L.

In speciation modelling, we have assumed that all the Mn entering the Queen and King Rivers has remained in the reduced manganous (Mn^{2+}) form. All the indications are that this is a reasonable assumption. For example, oxidation of Mn^{2+} by O_2 does not occur below pH 8 (Diem & Stumm 1984) and abiotic oxidation of Mn^{2+} proceeds more slowly than for Fe^{2+} taking an order of hours to days for completion (Pankow & Morgan 1981). Below pH 7.5, any oxidation of Mn^{2+} must rely upon microbiological processes (Laanbroek 1990). While bacterially-induced oxidation of Mn^{2+} may be an important process in impounded waters where equilibria can be attained, Laxen et al (1984) concluded that the oxidation kinetics were such under the short residence time of Mn in cold-water rivers that speciation would be little affected. Consequently, the short residence time of waters in the Queen and King Rivers coupled with low pH and low ambient temperature (10°C) will determine that Mn behaves conservatively, remaining in the reduced state.

Fluoride

The role of F^- as an important complexer of Al have already been discussed but there is little information upon which to judge F complexes as a potential toxicants to aquatic life. Dutch guidelines (MHSPE 1994) provide for a limit value of 1500 µg/L total F and none are provided by Australia (ANZECC 1992) or the USEPA (USEPA 1986). South Africa (Roux et al 1996) has indicated chronic and acute effective values of 100 and 7000 µg/L total F in that order. Environment Canada is currently reviewing recommendations on fluoride[1] but Quebec (MENVIQ 1993; cited by MacDonald 1994) has established chronic and acute criteria values at 200 and 4000 µg/L total F respectively.

Under acid conditions in rivers, the majority of F^- will be complexed to Al, although the proportion will depend on the stoichiometry of these two elements and the slow kinetics which prevail with low pH conditions. Under the model scenarios for the Queen and King Rivers, almost all the F^- is complexed with Al. When pH increases (with the combination of dilution and proportionally higher neutralisation of acid drainage) OH^- competes with F^- for Al complexation leading to 20%–60% of total F as the free F^- ion (figs 5.28 & 5.29 and table 5.12). The toxicity of F will therefore depend on the relative toxicities of the fluoro-Al forms and the fluoride anion. There is no reason to expect the toxicity of fluoro-Al complexes to differ substantially from the equivalent hydroxy-Al forms but unfortunately there is insufficient known about either the toxicity of fluoro complexes or the fluoride ion to aquatic systems to draw any conclusions about the Queen and King Rivers for the modelled scenarios. If 200 µg/L total F is taken as the criterion for chronic toxicity, then this will only be met at dilutions of 3% or less with 80% of acid drainage neutralised to pH 6.5 or, around ≤10% dilution with 99% neutralised to pH 6.5. If pH 5.5 is used as an endpoint, then ≤200 µg/L total F is only met with conditions of median flow in the King and an operating power station.

Iron

If 1mg/L total Fe is taken as a water quality guideline (tables 6.2 & 6.10), then reference to table 6.11 indicates that Fe would be a limiting factor for biological recovery in the Queen until around 98% (by extrapolation) of acid drainage is neutralised. In the King, the lower

---

[1] http://www.doe.ca/cwq...h/tables/inorgan2.htm

stretches would achieve a total Fe concentration of <1 mg/L if 80% of acid drainage was neutralised and if 99% was neutralised, Fe would not be a constraint to recovery.

Table 6.10 Guideline values for total Fe (µg/L) to protect freshwater aquatic ecosystems

Conc (µg/L)	Comments	Reference
300	Quebec; chronic toxicity	MENVIQ (1993)[1]
300	Ontario; unfiltered sample	Environment Ontario (1989)[1]
300	Canada; national guideline; unfiltered sample	CCREM (1987)
300	Ontario; provincial water quality guideline	OMEE (1994)[1]
300	Alberta; maximum	Alberta Environment (1977)[1]
300	British Columbia; maximum	Pommen (1989)[1]; BCMOELP (1994)[1]
1000	United States; national guideline; chronic toxicity	USEPA (1986; 1990[1]; 1993[1])
1000	Manitoba; maximum for cool and cold water aquatic life	MDEWPSH (1988)[1]
1000	Saskatchewan; protection of aquatic life and wildlife	SDEPS (1988)[1]

[1] Cited by MacDonald (1994)

The assessment above of Fe as a limiting factor to recovery presumes of course that Fe is precipitated as ferrihydrite on the mixing of raw acid mine drainage with higher pH river water. However, full equilibrium conditions, given the acidic pH and low ambient temperature of the receiving waters, may not be attained and the model may under-estimate the concencentration of Fe in solution. In a bench study, however, EGI (MLMRC 1995c) found that at dilutions of AMD with Queen River water of 1:10 (corresponding to pH 2.75) and more, the proportion of Fe precipitated from solution increased but it is probable that this work was conducted at room temperature. Despite the problem of ascertaining the true Fe concentration in solution from speciation modelling, it is clear given the relative tolerance of aquatic organisms to Fe compared with other contaminants in mine drainage, that Fe is less of a constraint to biological recovery in the Queen and King than either Cu or Al.

Table 6.11 Boundary concentrations of total Fe (mg/L) in the Queen and King Rivers under maximum and minimum dilution and various scenarios

		Queen River		King River		
				Power station off		Power station on
pH endpoint	AD neutralised	Max	Min	Max	Min	Max
6.5 & 5.5	65	11.3	>24.5	1.66	6.52	0.133
	80	5.67	>12.5	0.91	3.33	0.076
	99	0.228	>0.396	0.083	0.163	0.012

Summary

- If fluoride is present in sufficiently high concentration in acid drainage to pose constraints to biological recovery in receiving river waters, then liming to pH 5.5 will have no affect on total fluoride concentration. Liming to pH 6.5 will significantly reduce total soluble fluoride, by the precipitation of fluorite, and F^- discharge loads to the Queen and King Rivers.
- Iron in mine effluent discharge from Mount Lyell poses less of a limitation to biological recovery in the Queen and King Rivers than either Cu or Al.

7 Conclusions and recommendations for future work

The findings contained in this report have important ramifications for the development of remediation strategies at Mount Lyell and, hence, for the biological recovery of the Queen and King Rivers. In particular, predictions of bioavailable Cu concentration in the King River indicate there is little scope for recovery unless almost all (>99%) of the acid drainage which can enter Haulage Creek is neutralised to pH 6.5. Additionally, the use of SX/EW technology in conjunction with neutralisation of raffinate to pH 5.5 confers less advantage in terms of countering copper toxicity in the Queen and King Rivers than neutralisation of acid drainage to pH 6.5 in the absence of SX/EW. Consequently, if SX/EW is to proceed no advantage will be gained for downstream ecosystem recovery unless all raffinate is neutralised to pH 6.5. However, the model also predicts that even if 99% of acid drainage is treated to pH 6.5, water quality in the Queen River may continue to hamper biological recovery due to the toxicological impact of Cu from the remaining untreated drainage.

Aluminium, another metal of concern for the recovery of the river system, was more difficult to evaluate because there is a high degree of uncertainty about the relative toxicities of Al species to aquatic organisms and because there is a paucity of data pertaining to background concentrations in the King River catchment. However, model predictions suggest that Al may reach tolerable concentrations if somewhere between 80% and 99% of acid drainage is neutralised to either pH 5.5 or 6.5, conditions under which Cu concentrations would continue to be a limiting factor.

The potential toxicological impacts of fluoride, manganese and iron were also examined. Total soluble fluoride is present in sufficiently high concentration in acid drainage to possibly pose a problem to biological recovery. Consequently, liming to pH 6.5 is recommended to promote fluorite precipitation during neutralisation of acid drainage. Manganese and iron concentrations in the mixes of acid drainage with river water were found to probably represent far less of a limitation to biological recovery in the Queen and King Rivers than either copper or aluminium.

The formulation of the model has been constrained to some degree by a lack of baseline data. For example, there is a paucity of data on the composition of unimpacted river water in the Queen and King catchments. This is surprising given the use that has been made, and is being made, of clean river water for mill supply at Mount Lyell. It is recommended, therefore, that the monitoring of the East and West Queen Rivers above the mining operation and of the King River above the confluence with the Queen River be undertaken as soon as practicable from which a water quality database be constructed. This will allow the results of remediation to be judged against a set of water quality guidelines and objectives and will account for the effects of important, naturally-occurring temporal, spatial and hydrological variations in water chemistry.

It is important to note that the validation of model predictions was outside the scope of this project. Clearly, however, there is a need to test the predictions provided under the modelled scenarios by laboratory-based mixing experiments and, if necessary, to adjust the model to take account of deviation. Given the indefinite number of mixing scenarios coupled with variation in the composition of mine waters and diluent, this is no simple task. Nevertheless, using the speciation methodology described here, and accounting for dilution of mine drainage as a function of distance from the source term, the model is flexible enough to allow for validation to be undertaken over a wide range of carefully specified conditions.

Further refinements to model predictions forming part of model validation would require the following studies:

- an improvement in the chemistry database (see above). This should include the characterisation of the the composition of mine waters emanating from the West Lyell waste rock dumps and from Magazine Creek so that if progressive remediation can be achieved, variability in the chemistry of acid drainage at Mount Lyell can be better understood;
- the Cu and Al complexing capacities of dissolved organic matter in Queen and King River water;
- an assessment of the importance of Cu sorption by (natural and mine water derived) oxy-hydroxides in influencing river water $Cu^{2+}_{(aq)}$ concentration under the modelled scenarios;
- the kinetics of chemical and mixing processes involving river water, neutralised drainage and acid drainage.

References

Alberta Environment 1977. *Alberta surface water quality objectives.* Water Quality Branch, Standards and Approvals Division, Alberta Environment, Alberta.

Alva AK, Edwards DG, Asher, CJ & Blamey FPC 1986. Relationships between root length of soybean and calculated activities of aluminium monomers in nutrient solution. *Soil Science Society of America Journal* 50, 959–962.

Anderson HA, Hepburn A, Miller JD, Stewart M, Ferrier RC & Walker TAB 1990. Humic substances of surface waters: Litter and soil through flow relationships in two forested ecosystems. *Analytica Chimica Acta* 232, 3–10.

Apte SC, Benko WI & Day GM 1995. Partitioning and complexation of copper in the Fly River, Papua New Guineau. *Journal of Geochemical Exploration* 52, 67–79.

Apte SC, Gardner MJ & Ravenscroft JE 1990a. An investigation of copper complexation in the Severn estuary using differential pulse cathodic stripping voltammetry. *Marine Chemistry* 29, 63–75.

Apte SC, Gardner MJ, Ravenscroft JE & Turrell JA 1990b. Examination of the range of copper complexing ligands in natural waters using a combination of cathodic stripping voltammetry and computer simulation. *Analytica Chimica Acta* 235, 287–297.

Australian & New Zealand Environment & Conservation Council (ANZECC) 1992. *Australian water quality guidelines for fresh and marine waters.* ANZECC.

Barrow NJ 1985. Reaction of anions and cations with variable-charge soils. *Advances in Agronomy* 38, 183–230.

Bigham JM, Schwertmann U, Carlson L & Murad E 1990. A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe (II) in acid mine waters. *Geochimica et Cosmochimica Acta* 54, 2743–2758.

Borgmann U 1983. Metal speciation and toxicity of free metal ions to aquatic biota. In *Aquatic Toxicology*, ed JO Nriagu, Wiley Series in Advances in Environmental Science and Technology Vol 13, J Wiley and Sons, New York, 47–72.

British Columbia Ministry of Environment, Lands and Parks (BCMOELP) 1994. *Approved and working criteria for water quality – 1994.* Water Quality Branch, Environmental Protection Department, British Columbia Ministry of Environment, Lands and Parks, Victoria BC.

Brown DS & Allison JD 1988. *MINTEQA1, an equilibrium metal speciation model: User's manual.* Report No. EPA/600/3-87/012, United States Environmental Protection Agency, Athens, Georgia.

Buckney RT & Tyler PA 1976. Chemistry of salt lakes and other waters of the sub-humid regions of Tasmania. *Australian Journal of Marine and Freshwater Research* 27, 151–163

Bureau of Meteorology 1996. *Monthly data for Queenstown (Copper Mines of Tasmania).* Climate and Consultancy Section, Tasmania and Antartica Regional Office of the Bureau of Meteorology. August 1996.

Burrows WD 1977. Aquatic aluminium: Chemistry, toxicology and environmental prevalence. *CRC Critical Reviews in Environmental Control* 7, 167–216.

Cameron RS, Ritchie GSP & Robson AD 1986. Relative toxicities of inorganic aluminium complexes to barley. *Soil Science Society of America Journal* 50, 1231–1236.

Canadian Council of Resource and Environmental Ministers (CCREM) 1987. *Canadian water quality guidelines.* Task force on water quality guidelines of CCREM.

Carpenter PD, Butler ECV, Higgens HW, Mackey, DJ & Nichols PD 1991. Chemistry of trace elements, humic substances and sedimentary organic matter in Macquarie Harbour, Tasmania. *Australian Journal of Marine and Freshwater Research* 42, 625–654.

Chakoumakos C, Russo RC & Thurston RV 1979. Toxicity of copper to cutthroat trout (*Salmo clarki*) under different conditions of alkalinity, pH and hardness. *Environmental Science and Technology* 13, 213–219.

Commission of the European Communities (CEC) 1978. *On the quality of fresh waters needing protection or improvement in order to support fish life.* Council Directive 78/659/EEC.

Copper Mines of Tasmania 1995. *Mt. Lyell mine redevelopment: Environmental management plan.* Thompson & Brett Pty Ltd. August 1995.

——— 1996. *Tailings management plan: Princess Creek tailings dam.* Thompson & Brett Pty Ltd. May 1996.

Cressey PJ, Monk GR, Powell HJK & Tennent D 1983. Fulvic acid studies:evidence for a polycarboxylate co-ordination mode at soil pH. *Journal of Soil Science* 34, 783–799.

Davis JA & Leckie JO 1978. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67, 90–107.

Deighton N & Goodman BA 1995. The speciation of metals in biological systems. In *Chemical speciation in the environment,* eds AM Ure & CM Davidson, Blackie Academic & Professional, Glasgow, 307–334.

Diem D & Stumm W 1984. Is dissolved Mn^{2+} being oxidised by O_2 in the absence of Mn-bacteria or surface catalysts? *Geochimica et Cosmochimica Acta* 48, 1571–1573.

Driscoll CT, Baker JP, Bisogni JJ & Schofield CL 1980. Effect of aluminium speciation on fish in dilute acidified waters. *Nature* 284, 161–164.

Environment Ontario 1988a. *Scientific criteria document for development of provincial water quality objectives and guidelines. Aluminium.* Water Resources Branch, Ontario, Canada

Environment Ontario 1989. *Provincial water quality objectives.* Ontario, Canada.

Garvie AM & Gibson DK 1994. *Monitoring hole installation and quantification of oxidation in a waste rock dump at the Mt. Lyell mine.* Report to Renison Goldfields Consolidated Limited. ANSTO.

Gu B, Schmitt J, Chen Z, Liang, L & McCarthy JF 1994. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environmental Science and Technology* 28, 38–46.

Hart BT 1974. *A compilation of Australian water quality criteria.* Australian Water Resources Council Technical Paper No. 7, Department of the Environment and Conservation and the Australian Water Resources Council, Australian Government Publishing Service, Canberra.

Hawke DJ, Powell KJ & Gregor JE 1996. Determination of the aluminium complexing capacity of fulvic acids and natural waters, with examples from five New Zealand rivers. *Marine and Freshwater Research* 47, 11–17.

Hem JD 1977. Reactions of metal ions at surfaces of hydrous iron oxide. *Geochimica et Cosmochimica Acta* 41, 527–538.

Hem JD 1989. *Study and interpretation of the chemical characteristics of natural water.* United States Geological Survey Water-Supply Paper 2254, 3rd edn, US Government Printing Office, Washington DC.

Hydro-Electric Commission (HEC) 1988. King River power development: Heavy metal diversion study. HEC Internal Report, Hobart, Tasmania.

Johnson CA 1986. The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochimica et Cosmochimica Acta* 50, 2433–2438.

Juste C & Delas J 1966. Influence de l'addition d'aluminium, de fer, de calcium, de magnésium ou de cuivre sur la mobilité électrophorétique, le spectre d'absorption infrarouge et la solubilité d'un composé humique. *Annals Agronomie* 18, 403–427.

Kerndorff H & Schnitzer M 1980. Sorption of metals on humic acid. *Geochimica et Cosmochimica Acta* 44, 1701–1708.

Kinniburgh DG & Jackson ML 1981. Cation adsorption by hydrous metal oxides and clay. In *Adsorption of Inorganics at Solid-Liquid Interfaces*, eds MA Anderson & AJ Rubin, Ann Arbor Science Publications, Ann Arbor, Michigan, 91–160.

Kinraide TB & Parker DR 1987. Assessing the phytotoxicity of mononuclear hydroxy-aluminium. *Plant, Cell and Environment* 12, 479–487.

Kinraide TB & Parker DR 1989. Nonphytotoxicity of the aluminium sulfate ion, $AlSO_4^+$. *Physiologia Plantarum* 71, 207–212.

Koehnken L 1996. *Macquarie Harbour: King River study.* Technical Report. Department of Environment and Land Management, Tasmania.

Kuiters AT & Mulder W 1993. Water-soluble organic matter in forest soils. I. Complexing properties and implications for soil equilibria. *Plant and Soil* 152, 215–224.

Laanbroek HJ 1990. Bacterial cycling of minerals that affect plant growth in waterlogged soils: A review. *Aquatic Botany* 38, 109–125.

Laxen DPH, Davison W & Woof C 1984. Manganese chemistry in rivers and streams. *Geochimica et Cosmochimica Acta* 48, 2107–2111.

Locher H 1995. *Sediment transport in the King River, Tasmania.* Cooperative Research Centre for Catchment Hydrology, Monash University Working Document 95/5, Co-operative Research Centre for Catchment Hydrology. Monash University.

MacDonald DD 1994. *Fraser River Action Plan: A review of environmental quality criteria and guidelines for priority substances in the Fraser River Basin.* DOE FRAP 1994-30, Environment Canada, Environmental Conservation Branch, Pacific and Yukon Region. March 1994.

McQuade Christopher V, Johnston John F & Innes Shelley M 1995. *Review of historical literature and data on the sources and quality of effluent from the Mount Lyell lease site.*

Mount Lyell Remediation Research and Demonstration Program. Supervising Scientist Report 104, Supervising Scientist, Canberra.

Manitoba Department of Environment and Workplace Safety and Health (MDEWPSH) 1988. *Manitoba surface water quality objectives.* Water Standards and Studies Section, Manitoba, Canada.

Meador JP 1991. The interaction of pH, dissolved carbon and total copper in the determination of ionic copper and toxicity. *Aquatic Toxicology* 19, 13–32.

Miedecke John 1996. *Remediation options to reduce acid drainage from historical mining operations at Mount Lyell, Western Tasmania.* Mount Lyell Remediation Research and Demonstration Program. Supervising Scientist Report 108, Supervising Scientist, Canberra.

Miller TG & Mackay WC 1980. The effects of hardness, alkalinity and pH of test water on the toxicity of copper to rainbow trout (*Salmo gairdneri*). *Water Research* 14, 129–133.

Ministère de l'Environnement du Quebec (MENVIQ) 1990. Critères de qualité de l'eau. EMA88-09, Gouvernement du Quebec, Quebec City.

Ministère de l'Environnement du Quebec (MENVIQ) 1993. Critères de qualité de l'eau (Modifications et nouveaux critères). EMA88-09, Gouvernement du Quebec, Quebec City.

Ministry of Housing, Spatial Planning and the Environment (MHSPE) 1994. *Environmental quality objectives in the Netherlands.* Risk Assessment and Environmental Quality Division, Directorate for Chemicals, External Safety and Radiation Protection, MHSPE. Samson-Sijhoff.

MLMRCL (The Mount Lyell Mining and Railway Company Limited) 1990. *Physical impact of tailings discharge on the Queen and King River system.* Report commissioned for the MLMRCL.

— 1995a. *Modelling of water quality in the Queen and King Rivers below the Mount Lyell mine.* Technical Information from Draft Report October 1993. Environmental Geochemistry International (EGI) Pty Ltd. May 1995.

— 1995b. *Acid mine drainage control.* Technical Information from Interim Report May 1991. Environmental Geochemistry International Pty Ltd. May 1995.

— 1995c. *Investigations of the effects of Mount Lyell tailings and acid drainage on the chemistry of the Queen and King Rivers, Tasmania.* Technical Information from Interim Report July 1991. Environmental Geochemistry International Pty Ltd. May 1995.

Neville CM & Campbell PGC 1988. Possible mechanisms of aluminium toxicity in a dilute, acidic environment to fingerlings and older life stages of salmonids. *Water, Air and Soil Pollution* 42, 311–327.

Ontario Ministry of Environment and Energy (OMEE) 1994. *Provincial water quality objectives and guidelines.* Toronto, Ontario.

Pankow JF & Morgan JJ 1981. Kinetics for the aquatic environment. *Environmental Science and Technology* 15, 1306–1313.

Parent L, Couture P, Campbell PGC & Dubreuil B 1988. Sensibilité des alevins vésiculés du saumon Atlantique à l'acidité en présence et en absence d'aluminium inorganique. *Water Pollution Research Journal Canada* 23, 227–242.

Parker DR, Kinraide TB & Zelazny LW 1988. Aluminium speciation and phytotoxicity in dilute hydroxy-aluminium solutions. *Soil Science Society of America Journal* 52, 438–444.

Pettersson A, Hällbom L & Bergman B 1985. Physiological and structural responses of the cyanobacterium *Anabaena cylindrica* to aluminium. *Physiologia Plantarum* 63, 153–158.

Plankey BJ, Patterson HH & Cronan CC 1986. Kinetics of aluminium fluoride complexation in acidic waters. *Environmental Science and Technology* 20, 160–165.

Pohlman AA & McColl JG 1988. Soluble organics from forest litter and their role in metal dissolution. *Soil Science Society of America Journal* 52, 265–271.

Pommen LW 1989. *Approved and working criteria for water quality.* Water Quality Branch, British Columbia Ministry of the Environment, Victoria.

Radic N & Bralic M 1995. Aluminium fluoride complexation and its ecological importance in the aquatic environment. *The Science of the Total Environment* 172, 237–243.

Roux DJ, Jooste SHJ & MacKay HM 1996. Substance-specific water quality criteria for the protection of South African freshwater ecosystems: methods for derivation and initial results for some inorganic toxic substances. *South African Journal of Science* 92, 198–206.

Ryan DK & Weber JH 1982. Copper (II) complexing capacities of natural waters by fluorescence quenching. *Science and the Total Environment* 16, 866–872.

Sanjuan B & Michard G 1987. Aluminium hydroxide solubility in aqueous solutions containing fluoride ions at 50°C. *Geochimica et Cosmochimica Acta* 51, 1823–1831.

Saskatchewan Department of the Environment and Public Safety (SDEPS) 1988. *Surface water quality objectives.* Water Quality Branch, Regina, Saskatchewan.

Schnitzer M 1991. Soil organic matter: the next 75 years. *Soil Science* 151, 41–58.

Schnitzer M & Skinner SIM 1963. Organo-metallic interactions in soils. I. Reactions between a number of metal ions and the organic matter of a podzol Bh horizon. *Soil Science* 96, 86-93.

Senesi N 1992. Metal-humic substance complexes in the environment. Molecular and mechanistic aspects by multiple spectroscopic approach. In *Biochemistry of Trace Metals*, ed DC Adriano, Advances in Trace Substances Research, Lewis Publishers, Boca Raton, Florida, 429–496.

Shaw TL & Brown VM 1974. The toxicity of some forms of copper to rainbow trout. *Water Research* 8, 377–382.

Stortelder PB, van der Gaag MA & van der Kooij LA 1989. *Perspectives for water organisms: An ecotoxicological basis for quality objectives for water and sediment. Part 1. Results and calculations.* DBW/RIZA Memorandum N 89.016a, Institute for Inland Water Management and Waste Water Treatment, The Netherlands.

Swain LG & Holms GB 1985. *Fraser-delta area: Fraser River sub-basin from Kanaka Creek to the mouth. Water quality assessment and objectives.* Water Management Branch, British Columbia Ministry of Environment, Victoria, British Columbia.

Taylor Jeff R, Weaver Tamie R, McPhail DC 'Bear' & Murphy Nigel C 1996. *Characterisation and impact assessment of mine tailings in the King River system and delta, Western Tasmania.* Mount Lyell Remediation Research and Demonstration Program. Supervising Scientist Report 105, Supervising Scientist, Canberra.

Teasdale Peter, Apte Simon, Batley Graeme & Ford Phillip 1996. *The behaviour of copper in sediments and waters of Macquarie Harbour, western Tasmania.* Mount Lyell Remediation Research and Demonstration Program. Supervising Scientist Report 111, Supervising Scientist, Canberra.

Tipping E 1981. The adsorption of aquatic humic substances by iron oxides. *Geochimica et Cosmochimica Acta,* 41, 191–199.

Townsend GS & Bache BW 1992. Kinetics of aluminium fluoride complexation in single- and mixed-ligand systems. *Talanta* 39, 1531–1535.

United States Environmental Protection Agency (USEPA) 1986. *Quality criteria for water.* EPA 440/5-86-001, Criteria and Standards Division, Office of Water Regulations and Standards, Washington DC.

United States Environmental Protection Agency (USEPA) 1990. *Quality criteria for water-1989. (Updated 1986 water qualty criteria summary).* Criteria and Standards Division, Office of Water Regulations and Standards, Washington DC.

United States Environmental Protection Agency (USEPA) 1992. *Great Lakes water quality initiative.* Water Quality Branch, EPA Region V, Chicago, Illinois.

United States Environmental Protection Agency (USEPA) 1993. *Water quality criteria summary.* Ecological Risk Assessment Branch, Health and Ecological Criteria Division, Office of Science and Technology, Washington DC.

Vymazal J 1995. *Algae and element cycling in wetlands.* Lewis Publishers, Boca Raton, Florida.

Wilkinson KJ, Campbell PGC & Couture P 1990. Effect of fluoride complexation on aluminium toxicity towards juvenile Atlantic salmon (*Salmo salar*). *Canadian Journal of Fisheries and Aquatic Science* 47, 1446–1452.

Wilkinson KJ, Bertsch PM, Jagoe CH & Campbell PGC 1993. Surface complexation of aluminium on isolated fish gill cells. *Environmental Science and Technology* 27, 1132–1138.

Winner RW 1985. Bioaccumulation and toxicity of copper as affected by interaction between humic acid and water hardness. *Water Research* 19, 449–455.

Appendix

Table A1 Current predicted composition (mg/L) of river water mixed at various dilutions with 8% acid drainage neutralised to pH 6.5

Dilution series: 8% AD neutralised	**pH**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**F**	**SO4**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**	**DOM**
30%	3.12	39.94	101.50	4.60	0.95	12.00	6.946	895.30	75.541	33.607	39.900	28.664	3.600	7.00
15.7%	3.20	21.38	53.60	4.31	0.74	12.00	3.635	476.22	35.600	17.592	22.745	15.003	1.884	8.43
10%	3.26	13.98	34.50	4.20	0.65	12.00	2.315	304.41	20.950	11.209	14.515	9.558	1.200	9.00
3%	3.56	4.89	11.05	4.06	0.55	12.00	0.695	93.42	4.860	3.370	4.407	2.871	0.360	9.70
1%	3.96	2.30	4.35	4.02	0.52	12.00	0.232	33.14	1.450	1.130	1.519	0.960	0.120	9.90
0.3%	4.40	1.39	2.01	4.01	0.50	12.00	0.069	12.04	0.435	0.346	0.508	0.292	0.036	9.97
0.1%	4.77	1.13	1.34	4.00	0.50	12.00	0.023	6.01	0.175	0.122	0.219	0.101	0.012	9.99
Median flow in King River; power station on	4.47	1.30	1.77	4.00	0.50	12.00	0.053	9.96	0.366	0.268	0.357	0.225	0.028	9.98

Table A2 Predicted composition (mg/L) of river water mixed at various dilutions with 65, 80 and 99% acid drainage neutralised to pH 6.5

Dilution series: 65% AD neutralised	**pH**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**F**	**SO_4**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**	**DOM**
30%	3.31	79.75	101.50	4.60	0.95	12.00	2.997	709.64	24.388	33.607	16.555	11.144	3.600	7.00
15.7%	3.41	42.21	53.60	4.31	0.74	12.00	1.569	372.81	11.220	17.592	8.699	5.834	1.884	8.43
10%	3.52	27.25	34.50	4.20	0.65	12.00	0.999	238.55	6.467	11.209	5.568	3.718	1.200	9.00
3%	3.92	8.88	11.05	4.06	0.55	12.00	0.300	73.66	1.654	3.370	1.723	1.119	0.360	9.70
1%	4.32	3.63	4.35	4.02	0.52	12.00	0.100	26.55	0.542	1.130	0.624	0.376	0.120	9.90
0.3%	4.73	1.79	2.01	4.01	0.50	12.00	0.030	10.07	0.317	0.346	0.240	0.116	0.036	9.97
0.1%	5.00	1.26	1.34	4.00	0.50	12.00	0.010	5.36	0.126	0.122	0.130	0.042	0.012	9.99
Median flow in King River; power station on	5.01	1.61	1.77	4.00	0.50	12.00	0.023	8.44	0.133	0.268	0.150	0.091	0.028	9.98
Dilution series: 80% AD neutralised														
30%	3.43	90.23	101.50	4.60	0.95	12.00	1.958	657.64	12.432	33.607	9.492	6.534	3.600	7.00
15.7%	3.57	47.70	53.60	4.31	0.74	12.00	1.025	345.59	5.646	17.592	5.003	3.422	1.884	8.43
10%	3.71	30.74	34.50	4.20	0.65	12.00	0.653	221.21	3.323	11.209	3.214	2.181	1.200	9.00
3%	4.13	9.92	11.05	4.06	0.55	12.00	0.196	68.46	0.917	3.370	1.017	0.658	0.360	9.70
1%	4.53	3.97	4.35	4.02	0.52	12.00	0.065	24.82	0.321	1.130	0.389	0.223	0.120	9.90
0.3%	4.89	1.89	2.01	4.01	0.50	12.00	0.020	9.55	0.194	0.346	0.169	0.070	0.036	9.97
0.1%	5.09	1.30	1.34	4.00	0.50	12.00	0.007	5.18	0.085	0.122	0.106	0.027	0.012	9.99
Median flow in King River; power station on	5.21	1.69	1.77	4.00	0.50	12.00	0.015	8.04	0.076	0.268	0.096	0.055	0.028	9.98
Dilution series: 99% AD neutralised														
30%	4.49	103.50	101.50	4.60	0.95	12.00	0.642	591.77	0.386	33.607	0.545	0.694	3.600	7.00
15.7%	4.69	54.64	53.60	4.31	0.74	12.00	0.336	311.12	0.224	17.592	0.321	0.366	1.884	8.43
10%	4.83	35.17	34.50	4.20	0.65	12.00	0.214	199.26	0.159	11.209	0.232	0.235	1.200	9.00
3%	5.07	11.25	11.05	4.06	0.55	12.00	0.064	61.88	0.086	3.370	0.122	0.074	0.360	9.70
1%	5.16	4.42	4.35	4.02	0.52	12.00	0.021	22.63	0.057	1.130	0.091	0.028	0.120	9.90
0.3%	5.22	2.03	2.01	4.01	0.50	12.00	0.006	8.89	0.038	0.346	0.080	0.012	0.036	9.97
0.1%	5.22	1.34	1.34	4.00	0.50	12.00	0.002	4.96	0.033	0.122	0.077	0.007	0.012	9.99
Median flow in King River; power station on	5.91	1.79	1.77	4.00	0.50	12.00	0.005	7.53	0.012	0.268	0.027	0.010	0.028	9.98

Table A3 Predicted composition (mg/L) of river water mixed at various dilutions with 65, 80 and 99% acid drainage neutralised to pH 5.5

Dilution series: 65% AD neutralised	**pH**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**F**	**SO_4**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**	**DOM**
30%	3.31	79.17	101.50	4.60	0.95	12.00	7.500	719.78	24.478	33.607	19.196	17.107	3.600	7.00
15.7%	3.42	41.91	53.60	4.31	0.74	12.00	3.925	378.11	11.264	17.592	10.082	8.955	1.884	8.43
10%	3.52	27.06	34.50	4.20	0.65	12.00	2.500	241.93	6.52	11.209	6.449	5.706	1.200	9.00
3%	3.92	8.82	11.05	4.06	0.55	12.00	0.750	74.68	1.65	3.370	1.987	1.715	0.360	9.70
1%	4.33	3.61	4.35	4.02	0.52	12.00	0.250	26.89	0.53	1.130	0.712	0.575	0.120	9.90
0.3%	4.74	1.78	2.01	4.01	0.50	12.00	0.075	10.17	0.18	0.346	0.266	0.176	0.036	9.97
0.1%	5.00	1.26	1.34	4.00	0.50	12.00	0.025	5.39	0.09	0.122	0.139	0.062	0.012	9.99
Median flow in King River; power station on	5.01	1.60	1.77	4.00	0.50	12.00	0.058	8.51	0.13	0.268	0.170	0.137	0.028	9.98
Dilution series: 80% AD neutralised														
30%	3.44	89.51	101.50	4.60	0.95	12.00	7.500	670.12	12.493	33.607	12.742	13.873	3.600	7.00
15.7%	3.58	47.32	53.60	4.31	0.74	12.00	3.925	352.12	5.67	17.592	6.704	7.262	1.884	8.43
10%	3.71	30.50	34.50	4.20	0.65	12.00	2.500	225.37	3.33	11.209	4.297	4.628	1.200	9.00
3%	4.14	9.85	11.05	4.06	0.55	12.00	0.750	69.71	0.91	3.370	1.342	1.392	0.360	9.70
1%	4.54	3.95	4.35	4.02	0.52	12.00	0.250	25.24	0.31	1.130	0.497	0.467	0.120	9.90
0.3%	4.90	1.89	2.01	4.01	0.50	12.00	0.075	9.67	0.12	0.346	0.202	0.144	0.036	9.97
0.1%	5.09	1.30	1.34	4.00	0.50	12.00	0.025	5.22	0.08	0.122	0.117	0.051	0.012	9.99
Median flow in King River; power station on	5.21	1.68	1.77	4.00	0.50	12.00	0.058	8.13	0.07	0.268	0.121	0.112	0.028	9.98
Dilution series: 99% AD neutralised														
30%	4.48	102.61	101.50	4.60	0.95	12.00	7.500	607.21	0.39	33.607	4.568	9.776	3.600	7.00
15.7%	4.68	54.18	53.60	4.31	0.74	12.00	3.925	319.20	0.22	17.592	2.426	5.118	1.884	8.43
10%	4.81	34.87	34.50	4.20	0.65	12.00	2.500	204.40	0.16	11.209	1.573	3.262	1.200	9.00
3%	5.08	11.16	11.05	4.06	0.55	12.00	0.750	63.42	0.08	3.370	0.524	0.982	0.360	9.70
1%	5.20	4.39	4.35	4.02	0.52	12.00	0.250	23.14	0.05	1.130	0.225	0.331	0.120	9.90
0.3%	5.22	2.02	2.01	4.01	0.50	12.00	0.075	9.04	0.03	0.346	0.120	0.103	0.036	9.97
0.1%	5.22	1.34	1.34	4.00	0.50	12.00	0.025	5.01	0.03	0.122	0.090	0.038	0.012	9.99
Median flow in King River; power station on	5.92	1.78	1.77	4.00	0.50	12.00	0.058	7.65	0.01	0.268	0.058	0.080	0.028	9.98

Table A4 Predicted composition (mg/L) of river water mixed at various dilutions with 65, 80 and 99% acid drainage neutralised to pH 5.5 and with SX/EW

Dilution series: 65% AD neutralised	**pH**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**F**	**SO$_4$**	**Fe**	**Mn**	**Al**	**Cu**	**Zn**	**DOM**
30%	3.31	81.23	101.50	4.60	0.95	12.00	7.500	719.78	24.478	33.607	19.196	13.820	3.600	7
15.7%	3.42	42.99	53.60	4.31	0.74	12.00	3.925	378.11	11.264	17.592	10.082	7.235	1.884	8.43
10%	3.52	27.74	34.50	4.20	0.65	12.00	2.500	241.93	6.523	11.209	6.449	4.610	1.200	9
3%	3.92	9.02	11.05	4.06	0.55	12.00	0.750	74.68	1.659	3.370	1.987	1.387	0.360	9.7
1%	4.33	3.67	4.35	4.02	0.52	12.00	0.250	26.89	0.539	1.130	0.712	0.466	0.120	9.9
0.3%	4.74	1.80	2.01	4.01	0.50	12.00	0.075	10.17	0.189	0.346	0.266	0.143	0.036	9.97
0.1%	5.00	1.27	1.34	4.00	0.50	12.00	0.025	5.39	0.099	0.122	0.139	0.051	0.012	9.99
Median flow in King River; power station on	5.01	1.62	1.77	4.00	0.50	12.00	0.058	8.51	0.133	0.268	0.170	0.111	0.028	9.98
Dilution series: 80% AD neutralised														
30%	3.44	92.05	101.50	4.60	0.95	12.00	7.500	670.12	12.493	33.607	12.742	9.827	3.600	7
15.7%	3.58	48.65	53.60	4.31	0.74	12.00	3.925	352.12	5.674	17.592	6.704	5.145	1.884	8.43
10%	3.71	31.35	34.50	4.20	0.65	12.00	2.500	225.37	3.332	11.209	4.297	3.279	1.200	9
3%	4.14	10.11	11.05	4.06	0.55	12.00	0.750	69.71	0.914	3.370	1.342	0.987	0.360	9.7
1%	4.54	4.04	4.35	4.02	0.52	12.00	0.250	25.24	0.317	1.130	0.497	0.332	0.120	9.9
0.3%	4.90	1.91	2.01	4.01	0.50	12.00	0.075	9.67	0.127	0.346	0.202	0.103	0.036	9.97
0.1%	5.09	1.30	1.34	4.00	0.50	12.00	0.025	5.22	0.080	0.122	0.117	0.038	0.012	9.99
Median flow in King River; power station on	5.21	1.70	1.77	4.00	0.50	12.00	0.058	8.13	0.076	0.268	0.121	0.081	0.028	9.98
Dilution series: 99% AD neutralised														
30%	4.48	105.76	101.50	4.60	0.95	12.00	7.500	607.21	0.396	33.607	4.568	4.770	3.600	7
15.7%	4.68	55.82	53.60	4.31	0.74	12.00	3.925	319.20	0.228	17.592	2.426	2.499	1.884	8.43
10%	4.81	35.92	34.50	4.20	0.65	12.00	2.500	204.40	0.163	11.209	1.573	1.593	1.200	9
3%	5.08	11.48	11.05	4.06	0.55	12.00	0.750	63.42	0.083	3.370	0.524	0.481	0.360	9.7
1%	5.20	4.49	4.35	4.02	0.52	12.00	0.250	23.14	0.057	1.130	0.225	0.164	0.120	9.9
0.3%	5.22	2.05	2.01	4.01	0.50	12.00	0.075	9.04	0.038	0.346	0.120	0.053	0.036	9.97
0.1%	5.22	1.35	1.34	4.00	0.50	12.00	0.025	5.01	0.033	0.122	0.090	0.021	0.012	9.99
Median flow in King River; power station on	5.92	1.81	1.77	4.00	0.50	12.00	0.058	7.65	0.012	0.268	0.058	0.042	0.028	9.98