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Removal of Dissolved Copper and Iron at the Freshwater–Saltwater Interface of an Acid Mine Stream

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The King River, Tasmania, contains elevated levels of heavy metals, in particular copper, a result of the discharge of mine tailings and acid mine water from the Mt Lyell copper mine, which operated until late 1994. Samples were collected from the lower King River in July 1994, over a 48-h period, during which time the power station at the head of the river was off for the first 24 h. Saline water was observed in the delta region during this low flow period, and dissolved iron and copper were found to exhibit nonconservative behaviour with salinity. Removal of dissolved copper, as the river enters the harbour, was confirmed by laboratory experiments. The removal mechanism appears to be dependent on rapid pH increases and the formation of amorphous iron flocs which occur in the estuary, and results in a significant proportion of dissolved copper being removed from solution. © 1997 Elsevier Science Ltd

Keywords: iron removal; copper removal; acid mine drainage; estuarine; simulation; Macquarie Harbour.

The Mt Lyell copper mine operated at Queenstown on Tasmania's west coast until its closure in late 1994. Over a century of mining on this site resulted in the production of more than 100 million t of mine tailings and smelter slag, and unknown quantities of acid mine drainage (AMD) which were discharged into Macquarie Harbour via the King and Queen Rivers (Fig. 1). During mine operation the King River (below its confluence with the Queen River) and the Queen River both had a low pH and high particulate load and elevated levels of several heavy metals, particularly copper. As a consequence, mine tailings have formed sediment banks along the length of the rivers and an extensive delta at the mouth of the King where it enters Macquarie Harbour (Koehnken, 1996).

Above its confluence with the Queen River, the King River has been shown to contain baseline levels of heavy metals (DoE, 1975; Carpenter *et al.*, 1991). In 1991 the King River was dammed at Crotty, approximately 7 km above its junction with the Queen River. This resulted in formation of the Hydro Electric Commission (HEC) storage, Lake Burbury, and its associated power station, which is situated 500 m above the junction of the King and Queen Rivers (Fig. 1). Flow conditions in the King River have been altered by building the dam and are now highly dependent upon operation of the power station.

Macquarie Harbour is a large estuarine body with a three layer structure consisting of a surface low salinity layer, a deep marine saline layer and a layer of intermediate salinity which has a long residence time in the harbour (Cresswell *et al.*, 1989). The harbour is essentially a large land-locked bay and has two major freshwater inputs, the King and Gordon Rivers. The Gordon River enters the southern harbour; however, despite draining a metalliferous region, its catchment area is relatively undisturbed by mining activity and contains heavy metal concentrations representative of background levels (Carpenter *et al.*, 1991).

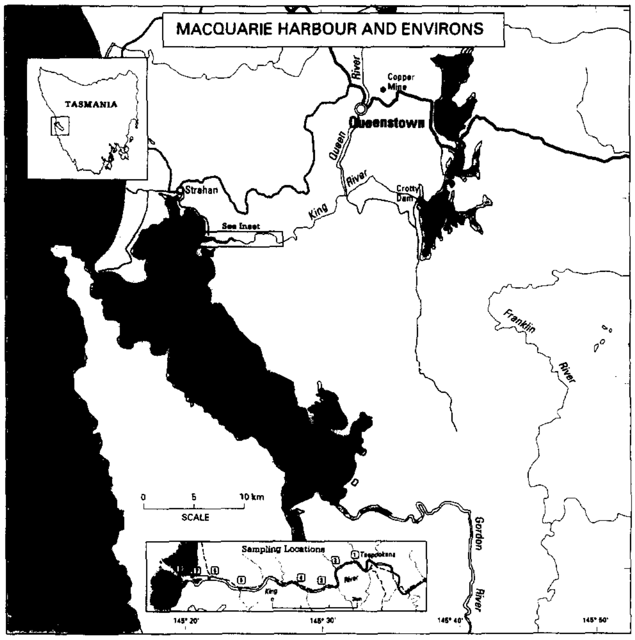

Fig. 1 Locality map showing the King River and surroundings with sampling locations and delta region inset.

Macquarie Harbour is a major tourist destination, and currently used as a recreational area, as well as being the site of several commercial fish farms. There has been concern for many years about the effects of elevated copper and other metals on the fish in the harbour and several surveys (DoE, 1975; Carpenter *et al.*, 1991; Koehnken, 1996) have been carried out to determine the distribution of these metals. Dissolved copper concentrations in parts of the harbour exceed established water quality guidelines for the protection of aquatic ecosystems (US EPA, 1985; ANZECC, 1992), and have also been shown to exceed the concentration of ligands available for strong copper complexation (Carpenter *et al.*, 1991). Owing to the commercial and recreational significance of the area, it is important to identify any mechanisms which may exist for removal of dissolved copper. This is particularly important as closure of the Mt Lyell mine is expected to result in an increase in metal concentrations, since while AMD from the site will continue, discharge into the Queen River will no longer be treated with lime.

The behaviour of dissolved copper in estuaries has not been well described until recently, due to difficulties in sampling without contamination and developing suitably sensitive methods for analysis of low metal concentrations. A recent study of six relatively unpolluted Texas estuaries using clean room techniques (Benoit *et al.*, 1994) found that the behaviour of copper varied widely in each estuary and that no simple variation of copper with salinity could be established. However, in acid mine streams, which have lower pH, a distinct loss of copper is observed with increasing salinity (Foster *et al.*, 1978; Johnson & Thornton, 1987). A number of explanations for removal of dissolved copper have been posed and include the effects of increasing salinity, increasing pH and adsorption onto particulate and colloidal materials (Lion *et al.*, 1982; Bourg, 1983; Johnson, 1986).

Although studies have been carried out to determine the distribution of metals in the King River and Macquarie Harbour, none have looked at the processes occurring at their interface. This paper will focus on a snapshot study, conducted prior to mine closure, which investigates the behaviour of copper and iron in the interfacial region where King River and Macquarie Harbour waters begin mixing. Results obtained from samples taken in the field are compared with those obtained from simulated mixing performed in the laboratory with representative samples of the two end-members.

Experimental

Study site

The King River flows about 30 km from Lake Burbury, an HEC storage and associated power station, into the north-eastern end of Macquarie Harbour (Fig. 1). Prior to construction of the HEC storage in 1991, the river was subject to frequent flooding. Operation of the power station has led to lower, more regulated flow in the river, and periods of very low flow when the power station is off.

Sampling

Water samples (2×200 ml) were collected from the river at 4 h intervals, over a 48-h period in July 1994. Grab samples were taken from 5 cm below the water surface, rinsing the bottle several times before taking the final sample. Bottom samples were collected using a sampler designed in our laboratory, which sampled water from a single depth, 30 cm above the river bed. Samples were taken at eight sites extending approximately 6 km upstream of the King River delta (Fig. 1). During sampling, the power station was turned off for the first 24 h and on for the second 24 h. Samples for metal analysis were filtered through 0.45 µm (200 ml) and 0.2-µm filters (~50 ml), acidified (10% HNO_3), and stored in acid-leached high density polyethylene bottles. Samples for acidity and salinity analysis were left unfiltered and analysed as soon as possible on return to the laboratory. A small sample (15 ml) was filtered and refrigerated for analysis by anodic stripping voltammetry (ASV).

Salinity, pH, temperature, time, depth and dissolved oxygen were measured *in situ* at all sites using a Hydrolab® H_2O® Multiprobe and Surveyor® 3 Display Logger. Throughout the sampling period, water level in the river was recorded by a continuous recording station in the sampling region.

Analytical methods

Dissolved copper (324.7 nm), iron (248.3 nm) and manganese (279.5 nm) in the 0.45 µm- and 0.2 µm-fractions, were determined by flame atomic absorption (Varian SpectrAA-600) using an air-acetylene flame. Standards were prepared by dilution of commercially available atomic absorption standards with 10% HNO_3.

Labile copper at pH 4.6 was determined by ASV using a portable Chemtronics PDV 2000 with a mercury plated glassy carbon electrode (Hall & Vaive, 1992).

Acidity is defined as the capacity of a water to react with a strong base to a designated pH, and is expressed as mg $CaCO_3$ per litre (Franson *et al.*, 1991). Total acidity was determined by automatic titration with standardised NaOH (0.005 M) using an Orion pH/ISE (EA 940/960) system. NaOH was added in small increments to a phenolphthalein endpoint (pH 8.3), which was determined using a pH electrode. As particulates were considered to contribute to the natural acidity of a sample, unfiltered samples were used.

Salinity was determined *in situ*; however, these values were confirmed in the laboratory as samples were not always collected from exactly the same depth at which the Hydrolab measurements were made. The chlorinity of each sample was determined by potentiometric titration with $AgNO_3$ using the first derivative method to determine the endpoint. Titrations were performed using an Orion 940/960 system with a silver wire indicator electrode and Ag/AgCl double junction reference electrode (Stark, 1996). Salinity was calculated from chlorinity using the Practical Salinity Scale (UNESCO, 1981).

The particulate load was determined by filtration of 200-ml samples through preweighed 0.45 μm cellulose acetate filters which were subsequently dried and reweighed.

Mixing experiments

In order to investigate further the behaviour of dissolved copper and iron in the mixing zone, an experiment was designed after Sholkovitz (1976). Ten litre samples, representative of the King River and Macquarie Harbour end-members, were collected during the sampling period. Filtered (0.45 μm) and unfiltered portions of these samples were mixed to give 13 mixtures within the salinity range, S = 0-21.6. Samples were allowed to equilibrate for 48 h before being filtered (0.45 μm) and analysed for iron, copper and manganese as described above.

Material retained on the filters following experiments with filtered water was also analysed for copper, iron and manganese following digestion using an AIM 500 Block digester. Filters were placed in test tubes with 5 ml of concentrated HNO_3. The temperature was stepped to 30°C and held for 30 min, and then to 100°C for 240 min. Following digestion, samples were diluted to 50 ml with deionized water.

Results and Discussion

Physicochemical measurements

Operation of the power station resulted in high flow conditions (~77 $m^3 s^{-1}$) in the river during which the entire sampling zone was nonsaline.

Under low flow conditions (~3.2 $m^3 s^{-1}$) the sampling zone was tidal and saltwater was observed at stations 7 and 8 in the delta. Samples taken during this period were found to vary in salinity between S = 0.09 and 22.4, the latter being considered representative of the final salinity in the surface layer of water circulating in Macquarie Harbour. It should be noted though, that salinity in this layer varies greatly depending on freshwater inflows and wind conditions, with mixing being predominantly wind driven (Koehnken, 1996). Saline water entered the delta underneath the outflowing freshwater and a distinct interface between the fresh and saltwater layers was observed. The depth of saltwater decreased as it approached the freshwater region, a characteristic of a salt wedge estuary. During the first 24 h of sampling, saltwater penetrated further upstream into the delta with time under the combined influence of low river flow and tidal changes. However, once the power station was turned on, increased flow dominated and the mixing zone was pushed out toward the harbour. The delta was found to be quite shallow close to the river mouth (~0.8 m), while near the delta's edge a sharp increase in depth occurred (~7.5 m).

Average values are shown for dissolved copper and iron, pH, acidity, temperature and sediment load in the river, both before and during operation of the power station (Table 1). The concentrations of dissolved iron and copper observed in the King River during this study are comparable with values found in other work (Watson & Roberts, 1979; Fuller *et al.*, 1989; Carpenter *et al.*, 1991; Koehnken, 1996). Clearly the metal concentrations in the river are similar before and during power station operation. However, because of the increased volume of water, the total flux of dissolved metals into the harbour is more than twenty times greater when the power station operates.

In the period immediately following restarting of the the power station, a maximum in all parameters was observed briefly. This observation was unexpected as water from the HEC catchment is relatively unpolluted and dilution of King River water should result in decreased metal concentrations.

The maximum coincides with remobilization of the mine tailings which have settled upstream under the influence of lower flows (Locher, 1995). It is thought that while the tailings are settled, oxidation of the sulphidic material can occur, trapping water of high acidity which can mobilize metals from the tailings (Koehnken, 1996). This water is then released once the settled material is disrupted by the restarting of the power station. Similar behaviour has been noted in the river prior to construction of the power station (Watson & Roberts, 1979), during disturbances of the river bed by natural flood events. In this case, the increased metal concentrations were also correlated with the increased suspended solids load.

Behaviour of dissolved iron and copper in the river

Acidity and dissolved metal concentrations generally

TABLE 1

Average values (± 10%) of temperature (°C), dissolved copper and iron (mg l^{-1}), acidity (mg $CaCO_3$ l^{-1}), pH, and sediment load (mg l^{-1}) in the King River during the sampling period.

River conditions	Temperature	[Cu]	[Fe]	Acidity	pH	Sediment load
Power Station off (24 h average)	8.6	0.6	1.2	13	4.8	50
Power Station on (restarting)	8.8	7.0	8.5	150	4.6	5000
Power Station on (during operation)	9.1	0.6	1.0	16	4.8	250

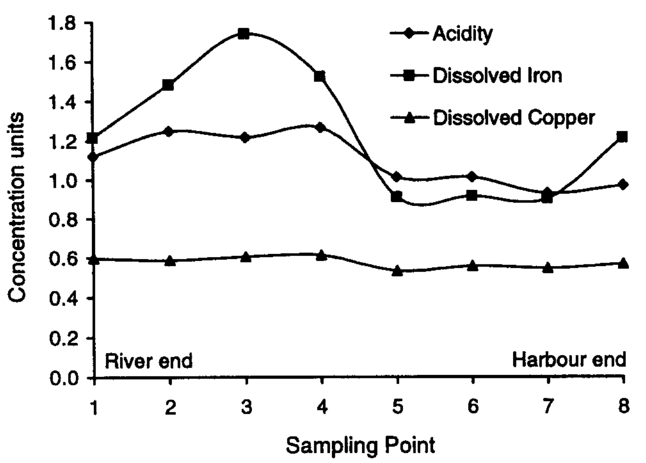

Fig. 2 Variation of acidity (mg $CaCO_3 l^{-1} \times 10^{-1}$), dissolved iron (mg l^{-1}), and dissolved copper (mg l^{-1}) in the lower King River approaching Macquarie Harbour.

decrease as the King River approaches the delta (Fig. 2), but the mechanism by which this occurs has not been investigated. Fluctuations, particularly in dissolved iron and acidity, occur along the river's length, with increases in concentration usually occurring at sites where there are large exposed banks of mine tailings (e.g. the delta). Smaller fluctuations in dissolved copper also occur at these sites. As iron is one of the major components of the tailings, it is expected to have much higher concentrations in leachate entering the river.

Partitioning of dissolved iron and copper in the river

For river samples, the concentration of copper passing through a 0.2 μm filter is the same as that passing through a 0.45 μm filter. This was in contrast to the behaviour of dissolved iron, where 60–80% of the iron passing through a 0.45 μm filter was retained by a 0.2 μm filter, suggesting that dissolved iron is dominated by colloids of particle size greater than 0.2 μm. From this it can be concluded that dissolved copper is not transported with dissolved iron (>0.2 μm) in the river.

ASV analysis shows that 50–80% of dissolved copper is ASV labile, although a preliminary analysis using electron paramagnetic resonance (EPR) indicates that copper is not present as the free (Cu^{+2}) ion. This suggests that the labile fraction must consist of copper complexes (inorganic or organic ligands), copper weakly bound to colloidal particles or particulate matter smaller than 0.45 μm, or a combination of these. A recent study of copper speciation in the Fly River, which also contains large amounts of particulate material from a copper mine, found that dissolved copper speciation was dominated by complexes with dissolved organic matter (Apte *et al.*, 1995). This might also be expected in the King River as its tributaries drain dense softwood and hardwood forests and button grass plains, and therefore contain high concentrations of humic material.

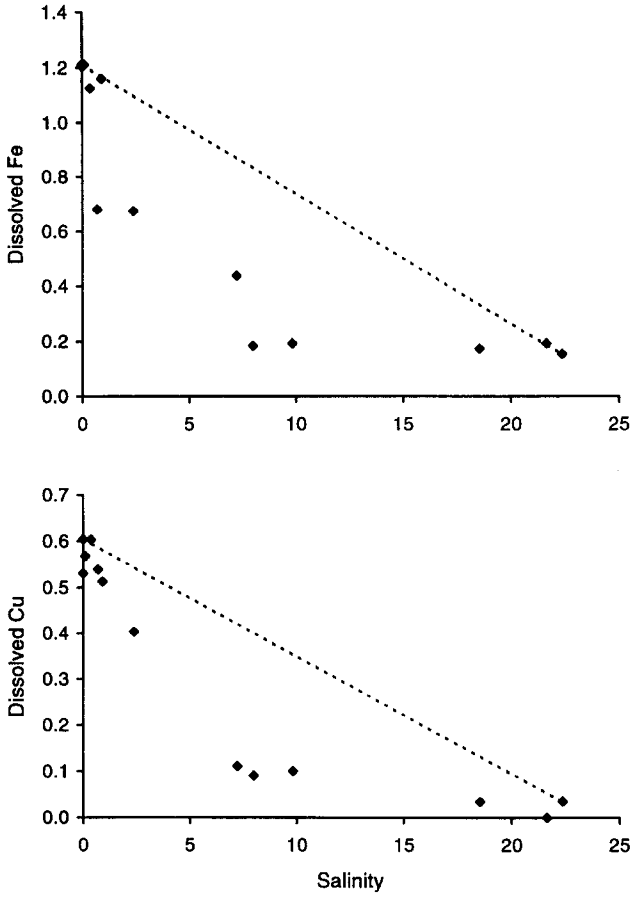

Fig. 3 Behaviour of dissolved iron (mg l^{-1}) and dissolved copper (mg l^{-1}) with salinity in the King River mixing zone.

Behaviour of dissolved copper and iron with salinity

Combining the results obtained for samples taken from the delta during the low flow period (Fig. 3), dissolved (0.45 μm) iron is shown to behave nonconservatively, deviating from the theoretical dilution line, with its removal essentially complete by salinity of 10. Similarly, dissolved copper (0.45 μm) appears to behave nonconservatively. The same behaviour is also observed for the 0.2 μm and ASV labile copper fractions.

Under certain tidal and wind conditions, water from the Gordon River (low salinity and dissolved copper) is known to remain relatively unmixed and travel up the western side of Macquarie Harbour to the mouth of the King River (Koehnken, 1996). Therefore, further experiments were required to show that the observed nonconservative behaviour of copper was not simply due to entrainment of water from this source.

Mixing experiments

Mixing experiments confirm the behaviour of dissolved copper and iron observed in the field; that is, that the metals are being removed from solution and nonconservative behaviour is not due to entrainment of water of low salinity and low copper concentration (Fig. 4). Comparison of the mixing experiments indicates that particulates play only a small part in

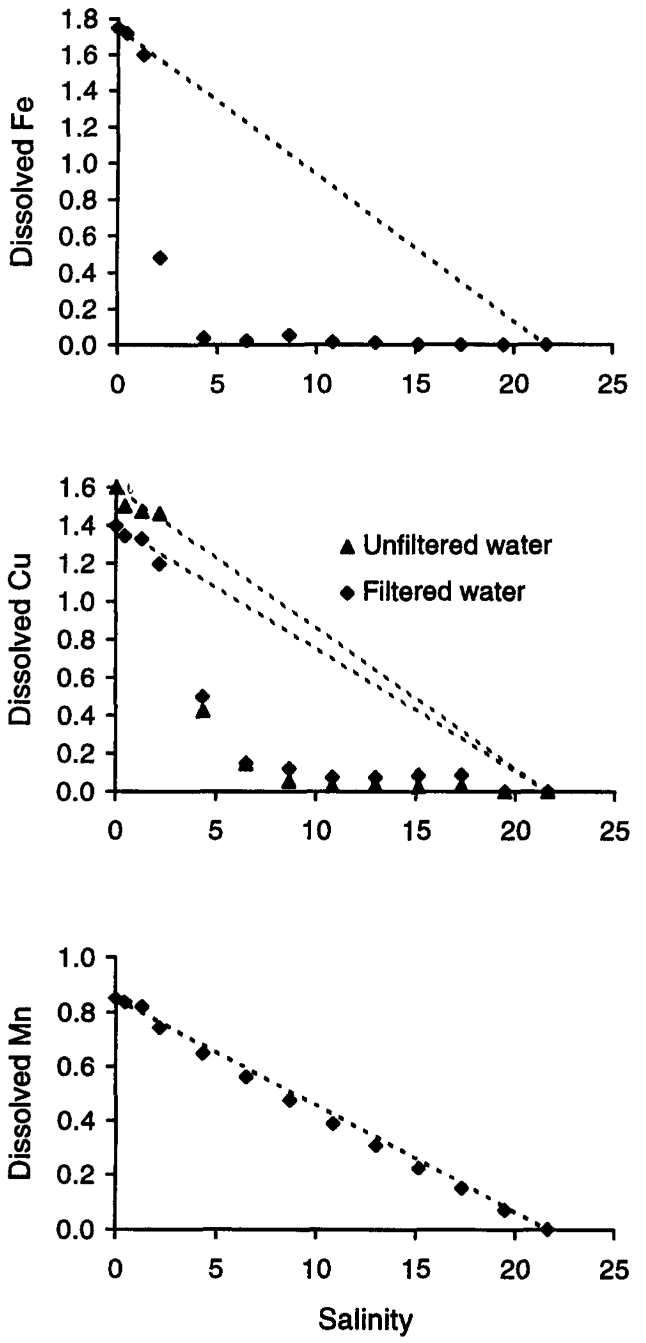

Fig. 4 Behaviour of dissolved iron (mg l^{-1}), dissolved copper (mg l^{-1}) (filtered and unfiltered water) and dissolved manganese in laboratory experiments using filtered King River and Macquarie Harbour water.

removal of dissolved copper from solution, as similar rates of removal are observed for experiments conducted without particulate material present. In interpreting the results of these experiments, it must be remembered that the conditions of mixing between river and seawater are not simulated exactly. The amount of particulate material present in each mixture is expected to be greater than that present in the estuarine environment, as the river flow slows upon meeting the harbour and so cannot maintain the same amount of suspended material. Therefore, particulates probably play a smaller role than indicated by experimentation. It is known, however, that suspended material is important in adsorbing dissolved metals in the freshwater region of the river (Koehnken, 1996), modulating the concentrations of dissolved copper reaching the mixing zone. In laboratory experiments, copper removal appears to be complete at a lower salinity than in the field. However, it is thought this is due to the extended reaction time of 48 h used for the laboratory study.

Removal of dissolved copper from the river appears to coincide with dissolved iron removal, within the limits of experimental error, indicating that removal of dissolved copper with increasing salinity may be associated with formation of the iron floc. Iron oxyhydroxides are known to provide sites for metal adsorption (Benjamin *et al.*, 1982; Johnson, 1986; Karlsson *et al.*, 1987) and have recently been shown to be able to adsorb more copper than there are available sites (Hart & Hines, 1995). This phenomenon is thought to be caused by a multiple-layer sorption mechanism. Manganese flocs are also known to be efficient scavengers of dissolved metals, although in this case, manganese is behaving conservatively and is therefore unlikely to be important in the removal of dissolved copper.

Removal processes

Experiments have indicated that particulate material does not significantly affect the removal of dissolved copper from the King River during mixing. Rather, dissolved copper removal appears to be related to the formation of iron flocs under conditions of increasing salinity. Filtration of samples taken from the river indicates that copper is not associated with large colloidal iron particles (> 0.2 μm) or present as colloidal copper (> 0.2 μm). It is therefore unlikely that copper associated with small colloidal iron particles (< 0.2 μm) or copper colloids (< 0.2 μm) are flocculating under the influence of increasing salinity.

It is thought that the rapid increase in pH associated with increasing salinity causes dissolved copper to be removed through adsorption of copper species onto recently formed amorphous iron (III) oxyhydroxide flocs or onto existing iron colloids which then flocculate.

Copper removal in the estuary of an acid mine stream has been observed in a another study (Johnson & Thornton, 1987), and in this case the authors concluded that dissolved copper removal was regulated by adsorption onto amorphous iron hydroxides. It is possible that this mechanism is also responsible for the removal of other dissolved metals from the King River which have not been investigated in this study.

Conclusions

Owing to the wide variety of conditions prevailing in the King River and Macquarie Harbour, it is difficult to make definitive statements about the fate of dissolved copper once it enters the harbour. It is evident, however, that a mechanism exists to remove a substantial proportion of dissolved copper once river and saltwater begin mixing. As this process is relatively independent of the particulate material in the river, it is envisaged that it will continue following mine closure, despite the prediction of higher dissolved copper concentrations. However, the extent to which removal will occur is unclear. It is possible that plumes of water with high concentrations of dissolved copper may occur in Macquarie Harbour, particularly following mine closure, as some river and harbour conditions are known to result in poor mixing. Preliminary results from harbour surveys following mine closure indicate that this may be the case, as King River plumes in the harbour now have increased concentrations of copper (Koehnken, 1995).

In late 1995 a new mine began operation on the Mt Lyell lease under strict environmental guidelines. The effects of previous mining on this site, however, are expected to persist for many years.

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