1 Introduction

The water quality and associated ecology of the Queen and King Rivers and the Macquarie Harbour in Western Tasmania (figure 1) has been adversely affected by mining activities at Queenstown over the past 100 years. Acidic and metal polluted drainage generated by groundwater and surface-water flow through oxidised sulphide-bearing rock, and the disposal of sulphidic tailings to the Queen River since 1916 have been the principal processes implicated in this environmental degradation. Widespread and severe erosion exacerbated by deforestation and locally-derived acid rain, as well as the disposal of sewage and municipal solid waste to the Queen River over part of its mining history, have contributed additional stress to the receiving environment. An estimated 95 Mt of sulphidic tailings, 1.4 Mt of smelter slag and approximately 10 Mt of top soil were disposed of to the Queen and King River system at Queenstown between 1916 and 1994 (Locher 1995).

Tailings and slag material were by-products from processing the copper-rich volcanogenic massive-sulphide deposits at Mount Lyell. While several discrete styles of mineralisation have been identified in the Lyell Mineral Field (Solomon 1989), the majority of the ore is pyrite-chalcopyrite dominated, and hosted by strongly deformed and brecciated, quartz-sericite-chlorite±carbonate altered felsic volcanic rocks of Cambrian age.

The unwanted sand to mud sized residue from the copper pre-concentration process and smelting activities has migrated down the Queen and King Rivers and has accumulated as (i) subaerial overbank deposits on the King River; (ii) subaqueous bottom sediments in the King River; and (iii) largely subaqueous deltaic deposits at the mouth of the King River in Macquarie Harbour. Estimates from Locher (1995) indicate that some 10 Mt of this material is currently located in the King River bed, roughly 3.4 Mt is stored in the King River banks, and much of the remainder has accumulated in the King River delta.

Overbank sediment deposits on the King River were deposited during storm events and range from 6 m above river level for the banks upstream, to less than 0.5 m near the delta. With the construction and operation of the John Butters hydro-electric power station on the Upper King River (figure 1) since October 1991, the influence of storm events on fluvial processes has been significantly dampened, and the once periodic inundation of the elevated sediment banks is now unlikely.

The subaerial portion of the King River delta currently covers approximately 2.5 km^2 and is bisected by a shallow channel through which the King River continues to flow. The maximum elevation across the subaerial delta at low tide is approximately 1.5 to 2.0 m, and a portion of the area is routinely inundated by generally unpredictable barometric tides in Macquarie Harbour. Tidal influences routinely cause a 30 to 50 cm water level rise over the delta, but complete inundation is reported by residents of Strahan to occur at least once per year. Operation of the John Butters Power Station has significantly reduced the incidence of widespread inundation of the subaerial delta. Tailings in the delta are largely comprised of fine to coarse sand, with an irregular, partially-cemented crust which appears to have developed on the more elevated sections. Key detrital components include siliceous rock fragments containing muscovite, chlorite and sulphides, sulphidic fragments, quartz vein material, carbonate, clay, organic debris and slag. The main sulphide minerals in the tailings include pyrite, chalcopyrite, bornite, sphalerite, galena, tennantite and tetrahedrite (Hince 1993).

The ubiquitous orange colouration of surficial tailings material in overbank and delta deposits reflects extensive chemical modification by oxidation, but the detailed chemical processes and long-term environmental impacts of the tailings accumulations are unknown.

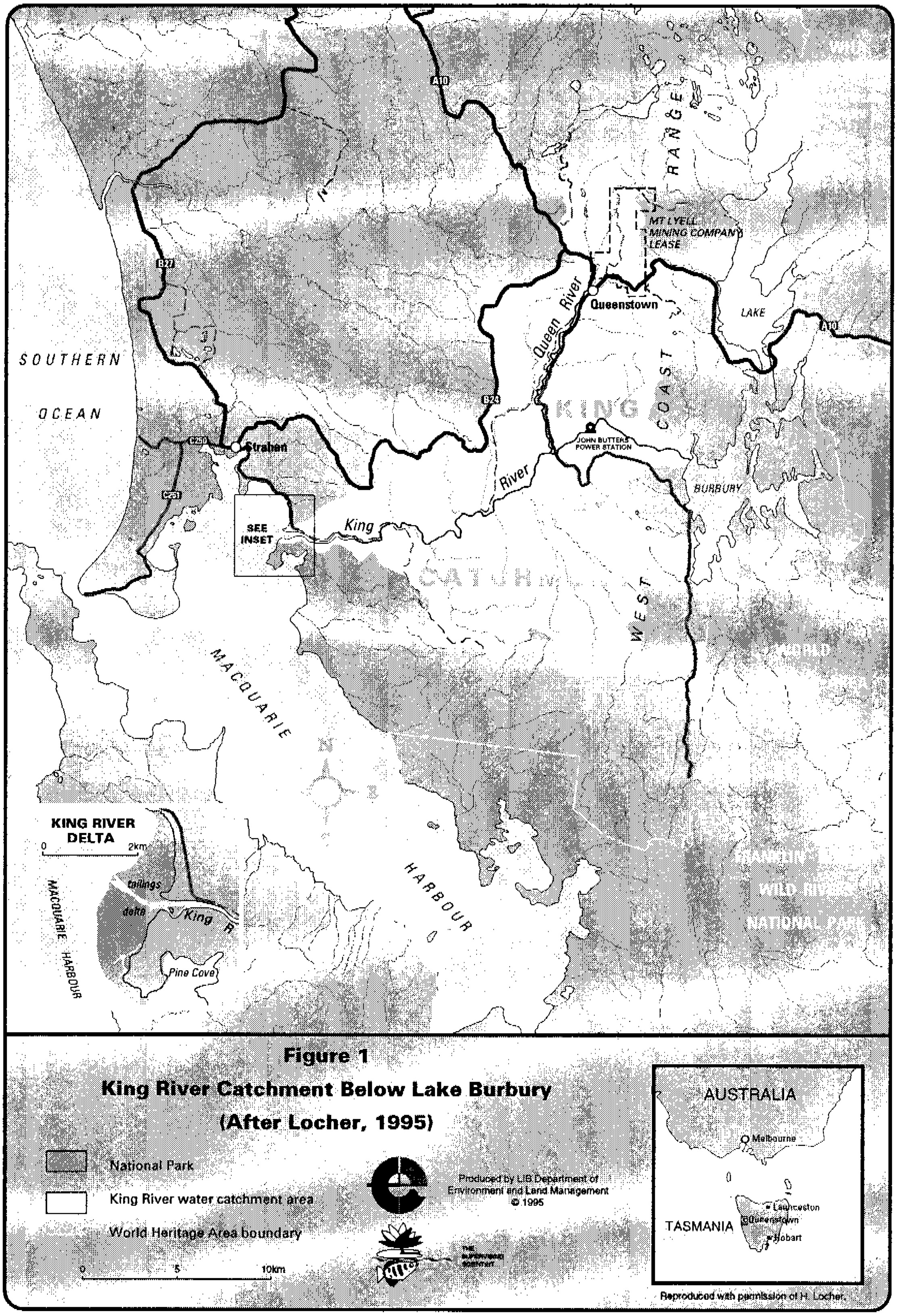

Figure 1
King River Catchment Below Lake Burbury
(After Locher, 1995)

Produced by LIS Department of Environment and Land Management © 1995

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The contribution of these deposits to the release of acid and heavy metal concentrations to surface-water has not been accurately determined.

The purpose of this study is to characterise the mineralogy and chemistry of the tailings material currently in storage in various fluvial environments in the Queen and King Rivers and associated delta, and to describe the potential of these tailings to cause further environmental impacts by the release of metals and acid. The effects of these mine wastes on water quality are compared to other key sources of water pollution entering the Macquarie Harbour (eg the Mount Lyell mining lease site). Such data permits the current and future acid and metal generating capacity of the tailings to be quantified, and appropriate management strategies to be devised.

Achieving these aims requires data on the speciation of environmentally significant metals in solid and aqueous phases. Metals fixed as solid phases may occur in primary crystal phases, as secondary amorphous or crystalline precipitates, or as compounds adsorbed onto pre-existing solid matter. In order to predict the flux of metals and acid into surface-water, a broad understanding of groundwater chemistry, hydrogeology and mineralogy of the tailings accumulations is required. Selective sampling of sediments and their pore water, in collaboration with the collection of fundamental hydrogeological, chemical and mass balance data is necessary to determine the processes and magnitude of acid and metal release. Fluid fluxes based on measured and modelled hydrogeological data are required in conjunction with analytical data on groundwater chemistry to calculate metal and acid release over unit areas for selected fluvial and deltaic settings. Channel cross sections provided by Locher (1995) and calculations of the perimeters of banks and delta by photo-analysis enables estimation of discharge areas, thereby permitting rates of discharge of metal enriched water to be determined. With estimated current discharge rates and a knowledge of the average composition of the tailings, predictions of the future impact of these deposits can be made. Geochemical modelling and leach tests can assist with an understanding of the fate of aqueous components as they discharge to surface-waters, and the likely environmental impacts if the tailings are physically disturbed. Key field observations and an understanding of acid generating processes can assist with the formulation of potential remedial strategies.

2 Previous work

The feasibility of exploiting the sulphidic tailings deposit in the King River delta for its sulphur and metal content has been examined by a number of companies. The Mount Lyell Mining and Railway Company Limited (MLMRCL) instigated an evaluation of the King River delta between 1969 and 1972. They reported an average Cu content of 0.16%, and estimated that 300 000 t of pyrite (4 to 7 wt%) were present in the top 1.5 m of exposed delta (Hince 1993). More recent exploration by Cottesloe Corporation (1987 to 1993) evaluated the tailings as a potential resource for sulphur, copper, gold, iron, cobalt, silver, barium, lead, zinc and molybdenum, with sulphur being the primary asset. Cottesloe calculated that the delta contained 5 to 7 Mt of pyrite. The inshore portion of the delta was estimated to contain 7.0 Mt of tailings which includes 0.5 Mt of pyrite concentrate, containing 200 000 t of S, 3000 t of copper, 400 000 kg of cobalt, and 400 kg of silver/gold. Reported copper grades averaged 1000 to 2000 ppm, and appeared to decrease away from the mouth of the river in a broadly concentric fashion. In the coarser grained oxidised crust on the delta, the copper sulphides were found to be largely bound together with other (secondary) material.

Auger drilling by Cottesloe (1987 to 1993) indicated that potentially economic components in the delta sediments are unevenly distributed, but tend to be segregated into the finer-grained, higher density portion of the tailings. Concentrations of cobalt, gold, barium, iron and sulphur all increase with decreases in the sediment particle size, and significant upgrading of the tailings resource could be achieved by rejecting the coarser half of the delta's inshore sediment. The composition and concentration of sulphide minerals in a typical tailings sample were reported as 5.57% pyrite, 0.21% chalcopyrite, 0.13% covellite, 0.11% sphalerite and 0.04% galena, and limonite coatings were recorded around grains of pyrite and chalcopyrite. Combined mineralogical and chemical analyses indicated that cobalt and sulphur occur chiefly in pyrite. Iron not present in pyrite occurs largely in limonite, siderite and magnetite. Gold was predicted to occur partially in its native state, with copper partly in chalcopyrite, and barium exclusively in barite. Cottesloe (1987 to 1993) estimated that 55% of the copper in the delta appears to be secondary, occurring as thin films of what was thought to be covellite/chalcocite on both sulphide and non-sulphide grains throughout the delta.

Five technical reports on matters pertinent to water quality, the impact of tailings and acid rock drainage (ARD) management strategies were produced by Environmental Geochemistry International (EGI) from 1991 to 1993 for the MLMRCL. This work indicated that most ARD has a low pH and contains elevated concentrations of Cu, Fe, Al, Mn and SO_4. EGI (1991a) identified and quantified the major individual sources of ARD and aqueous copper entering the King River and Queen River catchments. It was concluded that some 580 t of soluble copper was entering the Queen River annually. An order-of-magnitude less soluble copper was recorded entering the King River catchment from Comstock and Linda Creeks. Based on a tailings discharge rate of 200 L/s, EGI (1991a) estimated in 1991that 1650 t of copper was being disposed to the Queen River per year.

EGI (1991b) conducted a series of laboratory tests to examine the chemical consequences of mixing ARD and unpolluted river water (West Queen River) with or without fresh mine tailings, in an effort to simulate discharge operating scenarios associated with the Mount Lyell mine. Trials utilising mixtures of the three components demonstrated that the solubility of aluminium and copper was lower than predicted by dilution. Copper solubility appeared to be controlled by adsorption rather than precipitation reactions, with an estimated 130 mg of copper being adsorbed per kilogram of tailings. Lime (CaO) co-disposed with tailings appeared to be slowly dissolving during the process of mixing with ARD. Initially iron behaved as a conservative element during mixing and dilution, and must have been in its 2+oxidation state. Following high degrees of mixing and dilution, 62% of iron remained in solution. Experiments with mixtures of ARD and unpolluted West Queen River water showed that most elements behaved as would be predicted by quantitative dilution, except for the precipitation of some Fe.

EGI (1991b, 1993) concluded that the combined effects of neutralisation and adsorption by the tailings and dilution by the King River provide significant control on the concentrations of heavy metals entering Macquarie Harbour. A geochemical–surface-water flow numerical model (RIVCHEM) developed to evaluate the impact of acid mine drainage inputs from the Mount Lyell site also predicted that a significant portion of aqueous copper would be adsorbed onto tailings particles, and further suggested that all manganese remains soluble, most iron precipitates as ferrihydrite and most aluminium remains soluble (EGI 1993).

During 1991, 4000 to 5000 t/d of fresh tailings were being co-disposed with calcium oxide at a rate of approximately 12 t $CaCO_3$ equivalent/d. The short-term acid neutralising capacity (ANC) of this mixture, which was predicted by EGI (1991b) to be due to the calcium oxide, was 1.5 kg $CaCO_3$ equivalent/t tailings, and the long-term ANC was calculated at 13.3 kg $CaCO_3$ equivalent/t tailings, and assumed to be related to gangue minerals such as carbonates and oxides. EGI (1991b) predicted that tailings discharged from the mine displayed a net acid generation (NAG) in the order of 22 kg H_2SO_4 equivalent/t tailings. A relatively slow reaction time during the NAG tests suggested that the sulphides are likely to be slow to oxidise naturally.

Preliminary calculations (EGI 1991b) suggested that acid contributions to surface water from the subaerial tailings banks on the King River are 2 to 3 orders of magnitude less than the acid input from ARD sources at the Mount Lyell mine lease sites. EGI (1991b) estimated that acid release from material in bank storage is between 0.03 to 0.45 t of H_2SO_4 equivalent/d. These figures were based on a total surface area of between 0.3 to 0.5 km^2, an exposure depth of 3 cm and a sulphide oxidation rate of 0.5 to 5 g of pyrite/kg/year for tailings containing a few percent pyrite. This input compares to a figure of approximately 30 t of H_2SO_4 equivalent/d discharged directly from the Mount Lyell mine lease sites.

A brief study of the King River delta sediments was conducted by EGI (1991c), to evaluate the acid forming potential of selected samples, and provide a preliminary indication of the mineralogical association of copper within the sediments. The 2.0 km^2 of exposed delta tailings were described as generally orange-brown, highly oxidised at the surface (0 to 10 cm), and strongly acid generating when mixed with water (EGI 1992). Beneath the water table and oxidised surface layer (0 to 85 cm), tailings were grey and un-oxidised. Residual sulphides were reported to be stable, albeit reactive if oxidised. A general increase in sulphur was reported with depth in the delta sediments, due to a decrease in oxidation, but significant natural variability in total sulphur was observed (average $\approx$2 wt% sulphur in fresh tailings, with one sample up to 5.5 wt% S). EGI (1992) regarded the delta as a potential long-term source of acid and copper to Macquarie Harbour, and unlikely to be colonised by vegetation. Bulk chemical data indicated that copper, iron and manganese were significantly depleted in the surface 10 cm, and this was attributed to sulphide oxidation and leaching. The pH of natural pore water was measured at near neutral.

The acid neutralising capacity (ANC) of tailings below the water table was approximately 50% of the ANC for fresh tailings, and the net acid generation (NAG) procedure clearly demonstrated that sulphides in the tailings are reactive. EGI (1991c) concluded that sulphide oxidation was continuing at depth in the delta, and that physical disturbance would likely accelerate oxidation, and lead to the production of acid leachate. Based on extraction tests, EGI (1991c) suggested that most of the residual copper in the delta sediments occurs as sulphides, and predicted that, if oxidised and partially oxidised delta sediments were disrupted and deposited on the harbour floor, no major release of copper would occur.

Locher (1995) examined sediment transport in the King River, and provides a comprehensive physical framework for understanding river geomorphology and important baseline information regarding volumes and locations of sediment in storage in the King River river-system and delta. Her study showed that the banks of the King River can be up to 100 m wide and a maximum of 5 m in height above low water level. Locher estimated that they contain 3.4 Mt of tailings, and proposed that they developed in height and surface expression from existing levee banks. Locher determined the median grain size of the tailings throughout the history of disposal to be approximately 75 µm, with slag averaging 160 µm. A specific gravity of 2.9 was recorded for fresh tailings, and 2.7 for material in the sediment banks. Locher found copper to be an excellent indicator of mine-derived versus natural sediments (between 100 and 2500 ppm for tailings against natural background concentrations of 6 to 29 ppm).

Locher (1995) established that mine wastes have raised the river bed level by 5 m for much of the lower King River, and that approximately 7.3 to 10 Mt of sediment are stored in the King River bed. She determined that more than 80% of the estimated total bank sediments are stored between the Quarter Mile Bridge and Teepookana Bridge whilst greater than 80% of the estimated total bottom sediments are stored below the Teepookana Bridge.

According to Strahan historian Harry McDermott, the King River had a delta before mining activities commenced (Locher 1995). The delta has expanded gradually, and the growth of the subaerial portion, as determined from photographs dated 1953, 1974 and 1984, is presented in EGI (1991c). The vast majority of the tailings are believed to have been carried to the delta and the harbour floor (Locher 1995).

Hince (1993) conducted a physical and chemical evaluation of the tailings within the King River and delta, and provided insight into the distribution, mode of occurrence and behaviour of contained heavy metals. His work focussed on the development of a chemical leach procedure to assist determination of metal speciation in solid phases and evaluation of aqueous metal mobility. Hince determined that quartz and aluminosilicates comprised $\geq 70\%$ of the tailings, with sericite, biotite and chlorite comprising the bulk of the latter component. Pyrite ($\leq 5\%$), magnetite (1 to 2%), rutile and an orange iron-bearing precipitate make up the remaining significant phases. Non-oxidised tailings samples contain 3 to 7% sulphur, and oxidised samples contain about 0.2% sulphur. Mercury concentrations in sediment samples varied between 0.03 and 0.11 μg/g, and no trends were observed with depth. Hince (1993) also recorded the following anthropogenic contributions to the tailings mixture: methyl isobutyl carbinol, sodium isopropyl xanthate, and alkyl dithionocarbamate.

Three series of sequential and single-step extraction procedures were conducted on a range of oxidised and non-oxidised tailings samples to establish metal speciation. Hince (1993) concluded that the most suitable procedure consisted of a four-part single-step extraction process, utilising (i) water to recover soluble secondary phases; (ii) pH buffered hydroxylamine hydrochloride to extract metals adsorbed onto or included within iron and/or manganese-oxide bearing secondary precipitates; (iii) hydrogen peroxide to oxidise and dissolve sulphides; and (iv) hot, concentrated nitric acid to release metals associated with silicates.

In addition, Hince (1993) conducted simulated leach tests on subaerial and subaqueous tailings with deionised water and filtered Haulage Creek water. He concluded that exposed tailings have the capacity to release large quantities of acid as well as Cu, Zn, Fe and Mn, and that subaqueous tailings have the potential to be a sink for heavy metal accumulation. Further tests were recommended for subaqueous sediments stored under flowing water.

Examination of the geological literature for the Mount Lyell deposit has provided a broad mineralogical characterisation of all possible 'primary' mineral assemblages likely to be present in the tailings. Silicates include quartz (SiO_2), muscovite ($KAl_3Si_3O_{10}(OH,F)_2$), chlorite ($(Fe,Mg)_5Al_2Si_3O_{10}(OH)_8$), biotite ($K(Fe,Mg)_3AlSi_3O_{10}(OH,F)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$), epidote ($Ca_2FeAl_2Si_3O_{12}(OH)$), zircon ($ZrSiO_4$), sphene ($CaTiSiO_5$), fuchsite (chromian muscovite) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), and sulphides comprise pyrite (FeS_2), chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), tetrahedrite ($Cu_{12}Sb_4S_{13}$), tennantite ($Cu_{12}As_4S_{13}$), sphalerite (ZnS), enargite (Cu_3AsS_4), argentite (Ag_2S), galena (PbS), molybdenite (MoS_2), hexastannite (Cu_2FeSnS_4), arsenopyrite ($FeAsS$), digenite (Cu_2S), mawsonite ($Cu_6Fe_2SnS_8$), pyrrhotite (FeS), stromeyerite ($AgCuS$), linneaite (Co_3S_4), betechtinite ($Pb_2(Cu,Fe)_{21}S_{15}$) and bournonite ($PbCuSbS_3$). Carbonate minerals are widespread in some ore types, with siderite ($FeCO_3$) and dolomite

($(Ca,Mg)CO_3$) being most common. Accessory phases include magnetite (Fe_3O_4), chromite ($FeCr_2O_4$), hematite (Fe_2O_3), goethite ($FeO(OH)$), ilmenite ($FeTiO_3$), rutile (TiO_2), limonite ($FeOH.nH_2O$), barite ($BaSO_4$), anhydrite ($CaSO_4$), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), fluorite (CaF_2) and monazite ($(Ce,La,Th)PO_4$), and rare to trace amounts of native copper, metallic gold and electrum (Au–Ag alloy) have been reported.

The ecological impact of ARD on Macquarie Harbour has received little attention until recently. Acid drainage from the King River has been implicated as a potential contributing factor in a number of significant fish losses incurred by a fish farm in Macquarie Harbour (Wood 1991). If ARD is proven to be a key issue in local fish kills, it is likely that periodic flushing 'events' may have a more significant short-term impact on the ecology of the harbour than those caused by sustained but lower level acid/metal release.

Carpenter et al (1991) provided an excellent base of fundamental chemical and biochemical data on Macquarie Harbour water and sediments. One conclusion of particular relevance to this study is the identification of significant bacterial populations in harbour sediments. Similar microbial biomasses were reported from three sediment samples analysed, but differences in the relative abundance of phospholipid-derived fatty acids at each site indicated variable microbial community structures. Significant populations of anaerobic bacteria were present in sediments near the mouth of the King River, and biomarkers for sulphate reducing bacteria were present in all samples.

3 Field work

3.1 Introduction

Thirty-four person days of field work were conducted on the King River delta and sediment bank deposits between 28 July and 3 August 1995. The field component consisted of:

- installing and surveying mini-piezometers in key locations (see Sediment sampling) within the delta and sediment bank deposits;
- sampling groundwater from the piezometers and selected surface water;
- determining field chemical parameters for groundwater samples from piezometers (pH, redox potential (Eh), Conductivity (EC);
- filtering and acidifying groundwater samples from the piezometers for trace metal analysis;
- measuring groundwater levels and water level recovery rates in piezometers to establish hydrogeological conditions;
- drill testing and geological logging at selected locations;
- determining field chemical parameters (pH, Eh, EC) for groundwater and surface water from numerous localities (eg traverses on delta);
- extensive shallow auguring (0.1 to 1.5 m) for geological samples and hydrogeological data;
- limited surveying to assist with mass balance calculations based on aerial photo analysis.