The Hydrogeology and Geochemistry of Sediment Banks Contaminated with Mine Tailings in the King River, Tasmania

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Abstract

The King River in western Tasmania received approximately 100 million tonnes of sulphide-bearing tailings and slag from the Mt. Lyell copper mine at Queenstown by the early 1990s. These tailings and slag now contaminate riverbanks, bottom sediment and delta sediment in the King River and Macquarie Harbour. The tailings in the sediment banks and delta, in particular pyrite, have oxidised and reacted to generate acid and potentially toxic concentrations of many elements. The impact of the contaminated sediment in one riverbank, Bank D, on water quality in the King River is estimated using a combination of groundwater and geochemical methods. Groundwater flow, velocity and discharge are estimated in sediment banks using piezometric measurements and the geochemistry of groundwater and sediment is measured using a combination of analytical methods. Mass loadings of acid and elements for both summer and winter 1997 are calculated using groundwater discharges and measured groundwater geochemistry. In most cases, groundwater flow is perpendicular to and towards the river, although in the upstream end of the bank and close to the river flow can be away from the river. Estimated residence times of groundwater vary from less than one year to more than 20 years. Groundwater discharge from Bank D to the river is estimated to have been 8 m^3/day in summer and 19 m^3/day in winter. At most this represents only 0.04 vol.% of the flow in the King River at the time. The groundwater in the bank was acidic ($2.5 < pH < 6.6$) and acidity increased towards the river. In winter, groundwater was up to 2 units more acidic than in summer. Major elements in groundwater were dominated by iron and sulphate that result from the breakdown of pyrite, although high levels of aluminum (>100mg/l) were measured in some samples. Many heavy metals were detected in groundwater samples where concentrations were up to an order of magnitude higher in winter than summer. The sediment consisted mainly of quartz and lithic fragments, with pyrite and other sulphide minerals making up to 1 vol.%. In deeper parts of the bank, framboidal sulphide grains were observed, presumably the result of bacterial activity, and trapped up to more than 1000 ppm Co, Cu, Zn, Pb and Mn. Numerical modelling indicates that some dissolved elements, e.g., Fe, Si and possibly Ca, SO_4^{2-}, Mn and Al, are controlled by mineral solubility, whereas trace elements such as heavy metals may be controlled by adsorption. The overall mass loading of acid and metals from the groundwater and sediment in all riverbanks plus the delta of the King River, probably represents less than 1wt.% and 5wt.% of the total loading that results from the Mt. Lyell minesite at Queenstown.

Introduction

River systems can be severely contaminated by mining activity, e.g., direct disposal of mine tailings, waste rock and mine waters into the river systems, waste from smelting or other processing methods and drainage from waste rock piles, tailings impoundments and slag heaps on mine sites. The Queen and King Rivers in western Tasmania have been severely contaminated by waste material released in the past from the Mt. Lyell Copper Mine in Queenstown (e.g., Koehnken, 1997). An estimated 97 million tonnes of mine tailings and 4.5 million tonnes of slag were discharged into the Queen and King Rivers between 1916 and 1994 (Locher, 1997b). That material has been transported down the Queen River and now resides in bottom sediments and sediment banks of the King River and a large delta and bottom sediments in the Macquarie Harbour. Although the recent and current owners of the mine impound the tailings, the legacy of the historical mining activity results in continuing contamination from the mine site. Acidic, metal-rich water is pumped out of the mine, partially treated and released into Haulage Creek, a tributary of the Queen River. Piles of waste rock and slag at the minesite are sources of acid and metals that are leached by rain and ground water into the Queen River. As a result the Queen River is highly contaminated. For example, between December 1994 and April 1995, the Queen River downstream of the mine site had a pH of approximately 2.5 to 3.5 and median concentrations of 10,900 mg/l Cu, 12,500 mg/l Fe, 12,400 mg/l Mn and 26,200 mg/l Al, and this is after 3 to 7 times dilution of the element concentrations pumped directly from the mine (Koehnken, 1997). A median value of approximately two tonnes of copper per day enters the river system from the mine site, and up to nine tonnes of copper per day can enter the river system during storm events (Koehnken, 1997). The Queen River and lower reaches of the King River have been devoid of aquatic life for decades and the receiving body of water, the Macquarie Harbour, is contaminated with mine tailings, acid and dissolved metals from the outflow of the King River.

The environmental impact of past and present mining activity and strategies for remediating the environmental problems have been the subject of a major study sponsored, funded and directed by the Department of Environment and Land Management, Tasmania and the Office of the Supervising Scientist, Commonwealth of Australia. That study was the Mt. Lyell Remediation, Research and Demonstration Program (MLRRDP) and consisted of 16 projects that focussed on a wide range of topics. For example, the projects consisted of reviews of existing information, scientific studies of water and sediment quality in the river and harbour systems, fluvial processes, biological surveys and revegetation and other remediation strategies. The results of the individual projects were published in reports of the Supervising Scientist (Australia) as well as a summary report by Koehnken (1997).

The transport and environmental impact of mine tailings and slag that were released into the river system from the Mt. Lyell mining operation have been the subject of several recent studies. The sediment transport of the tailings was studied as part of the MLRRDP and a Ph.D. study by Helen Locher (Locher, 1997a; 1997b). The geochemistry, hydrogeology and environmental impact of mine-tailings in sediment banks and the delta of the King River have been studied as part of the MLRRDP (Taylor et al., 1996) and university research projects (e.g., Green, 1997; Hannan, 1996; Hooper, 1997).

The main focus of this chapter is to highlight the results of the geochemical and hydrogeological studies, and show how mine tailings contained within sediment banks impact on the water quality of the King River system. In particular, the results are summarised for one sediment bank to show how detailed studies can help in understanding the spatial and seasonal geochemistry and hydrogeology of sediment banks contaminated with sulphide-rich mine tailings.

Setting of the King River catchment

The King River catchment has an area of 809 km^2 and is situated in western Tasmania (Figure 1). The Mt. Lyell mine is in the Queen River subcatchment (area of 73km^2), the largest subcatchment in the King River catchment. Mine tailings, slag and mine water were pumped into Haulage Creek, a small tributary of the Queen River. Although tailings are now pumped into an impoundment and mine water is treated by the present mine operators, acidic and metal-rich mine water is still released into Haulage Creek. The Queen River flows through the town of Queenstown and drains into the King River, which then drains into the northern end of the Macquarie harbour, a stratified body of water with a surface area of 276km^2 (Figure 1).

The climate of the area is temperate with average temperatures of approximately 8°C to 22°C in summer and 2°C to 13°C in winter (e.g., Locher, 1997b). The annual rainfall ranges up to 2600 millimetres at the mine site to 1800 millimetres near the mouth of the King River (e.g., Taylor et al., 1996). Precipitation results from westerly winds that bring moisture picked up from the Indian Ocean and rise when they encounter the mountains of the West Coast Range of Tasmania.

Much of the King River catchment is densely forested (Blackwood, Myrtle, King Billy Pine and along the rivers, Huon Pine), although button grass plains are also present in upper reaches of the catchment (e.g., Locher, 1997b). The mine site was deforested during historical mining operation, a result of timber cutting for fuel, acid rain from pyritic smelting, loss of topsoil during heavy rain and frequent bushfires (e.g., Locher, 1997b). Soils consist mainly of yellow podzols common to areas underlain by siliceous rocks.

The Mount Lyell Copper deposit is hosted in the Cambrian Mount Read Volcanics (e.g., see Corbett, 1992). The geology, structure, stratigraphy, mineralogy and geochemistry of the deposit have been well studied (e.g., Walshe and Solomon, 1981; Taylor et al., 1996). The deposit consists mainly of massive pyrite + chalcopyrite and chalcopyrite + bornite ore that contains up to 50 vol.% pyrite, 15 vol.% sphalerite, 2 vol.% galena and many other ore minerals (e.g., chalcocite, covellite, digenite, enargite, molybdenite, tetrahedrite-tennantite and gold). Gangue and alteration minerals consist of quartz, barite, sericite and chlorite.

The geomorphology, hydrology and sediment transport and storage of the lower King River has been studied in detail by Helen Locher (Locher, 1997a; Locher, 1997b). The average flow rate in the Queen River (below the Lynchford camp) varied between 3.99 m^3/s and 6.98 m^3/s between 1988 and 1994 (Locher, 1997b, p. 19) and the maximum recorded rate was 107.6 m^3/s. In the King River (below the Queen River confluence) the average flow rate varied between 44.4 m^3/s and 61.7 m^3/s between 1992 and 1994 (Locher, 1997b, p. 19), with a maximum flow rate of 316 m^3/s in 1994. The water flow in the lower King River is now controlled by the John Butters Power Station, which is situated above the confluence of the King and Queen Rivers and was commissioned in 1992. There are fewer and less extreme flood events now, and that has affected the sediment transport in the King River (Locher, 1997b).

Mine tailings and slag are present in bottom sediments and sediment banks of the King River, although approximately 96% of the tailings and 19% of the slag have been flushed through the King River to its delta and the Macquarie Harbour (Locher, 1997b). Along the King River there are 21 sediment banks (Figure 2) that contained an estimated 3.4 million tonnes of tailings during 1993 to 1997 (Locher, 1997b). The bottom sediments in the lower 8 km of the

King River contained up to 10 million tonnes of tailings, resulting in the river bed being raised by up to 9m (Locher, 1997b). Upstream the sediment banks in the King River are mounded levee banks up to six metres above the average river level. They range in length from 250 m to 2820 m and in width from 10 m up to 140 m, and the estimated depth of tailings is between 1.25 m and 4.5 m (Locher, 1997b). The morphology of the banks changes downstream, where they become flatter and lower (approximately 1-3 m above average river level).

The hydrogeology and geochemistry of four banks (D, H, N and R; Figure 2), two of each bank type, and the King River delta were studied in 1996 (Taylor et al., 1996). Subsequently, one bank (Bank D; Figure 2) was studied in detail to learn more about the geochemical and hydrogeological variability in the banks and seasonal variability in groundwater flow and geochemistry (Baker et al., in preparation; Green, 1997; Green and McPhail, in preparation; Hooper, 1997). Bank D is a low, flat-topped bank approximately 2.5 km upstream of the mouth of the river. It is approximately 800 m long and varies in width from less than 15 m at the ends to approximately 100 m in the middle of the bank. It rises approximately 1.5 m to 2 m above average river level and the depth of mine tailings is on average approximately 3 m (Green, 1997).

Methods

A combination of hydrogeological and geochemical methods was used to study the impact the sediment banks on the water quality of the King River (Green, 1997; Hooper, 1997; Taylor et al., 1996). In addition, geophysical methods have also been used to study the water distribution and contamination in Bank D (Baker et al., in preparation). Hydrogeological methods allow the estimation of groundwater flow and discharge within sediment banks and geochemical methods allow the geochemistry of groundwater and sediment to be measured. The combination allows the prediction the mass loadings of acid and elements that are entering or leaving the river system from sediment banks. Detailed geochemical studies result in a better understanding of atmosphere-water-sediment interaction that is especially important in acid drainage environments.

As part of the studies highlighted in this chapter, fieldwork was conducted on Bank D three separate times: July-August 1995 (winter; Taylor et al., 1996) and February 1997 (summer) and June 1997 (winter; Baker et al., in preparation; Green, 1997; Green and McPhail, in preparation; Hooper, 1997).

Hydrogeology

A total of 33 piezometers were installed in 9 lines approximately perpendicular to the river (Figure 3). The piezometers consisted of 50 mm PVC pipe that had a slotted interval cut into the bottom 20 cm of each pipe. The slotted interval was covered by a sleeve of 100 µm nylon mesh and secured with tape at the top of the sleeve and a nylon plug at the bottom of the pipe. Holes were hand-augered into the sediment bank and the piezometers were inserted once the holes penetrated the water table by at least several tens of centimetres. Because the sediments are unconsolidated they collapsed around the bottom of each piezometer, preventing any packing and sealing of the screened interval of the piezometers. The holes near the top of the piezometers were packed using sediment from the augered hole. In some areas of the bank, nests of piezometers were installed to measure the water levels and quality as a function of depth. Piezometer depths varied between approximately 1 to 4 metres (Table 1). During installation the lengths of the piezometers were recorded and after installation, the relative elevations of were surveyed to approximately 1 cm accuracy.

Depth to the water level was measured in each piezometer using an electric water level tape. Using the surveyed elevations of the piezometer tops, the hydraulic head was calculated from the raw measurements for both summer and winter. Hydraulic conductivities were measured in the field and the laboratory. Field measurements were made using rising head tests, where the water was bailed out using disposable nylon bailers and the subsequent rise in the water level in the piezometer was measured periodically. The results were used to calculate hydraulic conductivities by the Hvorslev method (Hvorslev, 1951; e.g., see Fetter, 1994 pp. 247-251). Hydraulic conductivities were also measured in the laboratory using a constant-head permeameter (e.g., Fetter, 1994 pp. 103-107.); however they were approximately an order of magnitude higher than those measured in the field. The field measurements are preferred because it is likely that the samples used in the permeameter were disturbed during sampling and transport (e.g., vibrations could have broken up grains or cemented clumps; Hooper, 1997).

Grainsize and porosity of sediment were measured for core samples taken near eight of the nine series of piezometers installed in Bank D (Figure 3), the exception being the upstream end of the bank (Series I). Grainsize was measured using a combination of sieving and a laser dispersion technique for grainsize less than 80 µm. Porosity was measured by saturating segments of the core samples with water and then drying the samples to constant weight. The porosity was calculated from the known initial volume and mass of sediment plus water, the dry weight and assuming the density of water was 1.0g/cm^3.

Geochemistry

Sediments from the bottom of all the augered holes were sampled in order to study sediment and groundwater samples that were from the same areas and depths within the bank. The mineralogy of the samples was determined using conventional petrographic, electron microprobe and X-ray diffraction techniques. Partial geochemistry of the sediments was measured by digesting samples in hot nitric acid and measuring Fe, Mn, Al, Cu, Zn, Co and Pb. Selected samples were also subjected to sequential extraction (e.g., Tessier et al., 1979) to measure the speciation of trace metals in the sediments. The sequential extraction steps were (Green, 1997): i) exchangeable or leachable (1.0M $MgCl_2$), ii) acid soluble (1M NaOAc at pH = 5), iii) reduceable (0.04 M $NH_2OH \cdot HCl$ + 25 vol.% HOAc), iv) oxidisable (0.02 M HNO_3 + 30 vol.% H_2O_2 at pH = 2 and 85°C, followed by 30 vol.% H_2O_2 at 85°C and then 3.2 M NH_4Oac + 20 vol.% HNO_3) and v) immobile (concentrated HNO_3 at 85°C). Element concentrations in filtered and acidified extractions were analysed by Atomic Absorption Spectroscopy (AAS; major and minor elements) or High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS; trace elements).

Groundwater was sampled in summer and winter in all piezometers after purging at least 3 times. As quickly as possible, water samples were measured in the field for temperature, pH, Eh, Electrical Conductivity (EC) and then filtered through 0.45 µm cellulose acetate filters. Several preparation steps were subsequently taken. Parts of the samples were acidified with 1 M nitric acid for element analysis in the laboratory. Chemicals were added to separate parts of the sample to measure ferrous iron (orthophenanthroline), sulphide (Zn-acetate) or sulphate (barium chloride). In addition, chloride concentrations were measured using an ion specific electrode. All samples were stored in acid-washed HDPE bottles and transported to the laboratory in closed (i.e., dark) and ice-packed containers. Element concentrations in the filtered and acidified samples were measured using the same techniques used for sediment analysis plus UV-Vis spectrophotometry for dissolved silica.

Results and Discussion

Hydrogeology

The groundwater flow varied between summer and winter. In general the groundwater levels, i.e., hydraulic heads, were higher in Bank D compared with the river level at the times of measurement, indicating that groundwater was flowing to the river from the bank. The same was true for three other sediment banks (H, N and R; Figure 2) that were studied as part of Taylor et al. (1996). In Bank D, the hydraulic heads were approximately 10 cm to 50 cm higher in winter (i.e., June 1997), probably because of increased rainfall. The river level at Bank D, surveyed during the field trips in February and June 1997, varied by up to 20 cm, mainly following rainfall events but also because of the power needs of the John Butters Power Station upstream.

Contours of hydraulic head were calculated using the values from shallow piezometers, boundary conditions at the river's edge (average river level) and north of the bank (ponded water beside Lowana Road (Figure 4) and interpolation methods (i.e., kriging option in the computer program SURFER). The two ephemeral creeks shown in Figure 3 are omitted for simplicity. Contours are shown for summer and winter (Figure 4). Most of the contours are subparallel with the river's edge and hydraulic head decreases towards the river. During summer the measured water levels in some piezometers near the river's edge were lower than the river level. Those piezometers are in the upstream end of Bank D (lines F, G and H). This indicates that during some times of year (lower rainfall and/or increased river level) that Bank D groundwater could be recharged by river water. Not only does this have an effect on the groundwater flow in the bank, but it could also affect water and sediment compositions in the bank. For example, river water probably contains higher dissolved oxygen levels and different element concentrations than the groundwater. Increasing the oxygen levels in the sediment bank may increase acid generation in the bank and element concentrations in groundwater could be concentrated or diluted, depending on the relative concentrations of the river water. The changing geochemical conditions could also result in the dissolution or precipitation of minerals; e.g., oxygenated waters could oxidise and dissolve sulphide minerals and result in the deposition of iron oxyhydroxide minerals.

Groundwater discharge and velocity in the saturated zone within the bank can be estimated using Darcy's law, once the hydraulic conductivity, hydraulic gradients and porosity are known. Darcy's law is used to calculate specific discharge (e.g., Fetter, 1994, p. 145):

$$v = \frac{Q}{A} = K\frac{dh}{dl}$$

where v is the specific discharge (e.g., m/s), Q is the total discharge (e.g., m^3/s), A is the cross-sectional area of groundwater flow (e.g., m^2), K is the hydraulic conductivity (e.g., m/s) and dh/dl is the hydraulic gradient (e.g., m/m or dimensionless). The average linear velocity is calculated by dividing the specific discharge, v, by the porosity expressed as a fraction.

The values of hydraulic conductivity calculated from rising-head field tests range from 8.0×10^{-8} m/s to 9.6×10^{-6} m/s (Hooper, 1997), with an average of 2.6×10^{-6} m/s (19 measurements). These values are consistent with those of silty to fine sands (e.g, Fetter, 1994; p. 98), as are observed in the sediments. There are no clear spatial trends in the hydraulic conductivity in Bank D, although values generally increased from the upstream end of the bank to the downstream end.

Hydraulic gradients vary throughout Bank D and are estimated for areas between the measured hydraulic head values at the bases of the piezometers. Approximately horizontal gradients are estimated between the shallowest piezometers and vertical gradients are estimated from piezometer nests. In general, approximately horizontal hydraulic gradients increase as the river's edge is approached, as is seen by the closer spacing of the hydraulic head contours nearer the river (Figure 4). Hydraulic gradients perpendicular and closest to the river vary between approximately 0.007 and 0.022 towards the river in the summer, although in some parts of the bank (F, G and H series; Figure 4) the hydraulic gradients point away from the river, reflecting the recharge mentioned above. In winter, the approximately horizontal gradients steepen to between approximately 0.015 and 0.060 and at the time of measurement (June 1997) all gradients pointed towards the river. Vertical gradients were measured in several piezometer nests: C2 and C3; E2, E4 and E6; F1, F5 and F7; F2 and F6; F3 and F4; G3 and G4; H1 and H3 (Figure 3). Away from the river, vertical gradients were downward in both summer and winter, and greater in winter. Near the river (F1, F5 and F7; H1 and H3), the vertical gradients were near zero in both winter and summer in the F-line nest and changed from downwards in winter and slightly upwards in summer in the H-line nest. This reflects the decreased hydraulic heads in summer.

Measured porosity values vary between 40% and 54% and in general increased towards the upstream end of Bank D. The average grainsize of sediments ranged between 0.05 mm and 0.28 mm and in general decreased towards the upstream end of Bank D. In most cases, the samples were poorly sorted according to the calculated standard deviations of grainsize (i.e., $\sigma = 1.00\Phi - 2.00\ \Phi$) and classification scheme of Folk (1974).

Groundwater discharge to the river is calculated using the hydraulic conductivities, hydraulic gradients and Darcy's law. Summer and winter discharges are calculated by subdividing Bank D into sections corresponding to the piezometer lines (boundaries between sections are the midlines between the lines). The hydraulic conductivity for each piezometer series is an average of the measured values in that series and the summer and winter hydraulic gradients are calculated between the river's edge and the second row of piezometers along the bank. Flow is assumed to be horizontal only and the depth of the cross-sectional area of flow is assumed to be 4 m. The depth estimate is based on measured river channel depths at points above and below Bank D in 1988 and 1994 (Locher, 1997b, pp. 43-46). The results are listed in Table 2. The total groundwater discharge into the river from Bank D during the times of our measurements is estimated to be 8 m^3/day during summer (February 1997) and 19 m^3/day during winter (June 1997), reflecting the higher hydraulic gradients in the bank during winter.

Taylor et al. (1996) estimated the total groundwater discharge from Bank D, based on three piezometer measurements made in the winter of 1996, to be 93 m^3/day. This is approximately 5 times higher than the estimate of 19 m^3/day for winter 1997 in this study. Although there could have been a higher discharge in 1996, much of the difference is more likely attributable to the lower hydraulic conductivity found in this study. They assumed a value of $K = 1 \times 10^{-5}$ m/s, based on one rising-head test, whereas the average value found in this study was approximately 3 times lower ($K = 2.9 \times 10^{-6}$ m/s).

In order to evaluate the effect groundwater discharge has on the river water, it is necessary to know the river flow. Accurate river flow rates are unknown for February and June 1997. The mean annual flow of the King River (below the confluence of the Queen River) between 1924 and 1984 and after the commissioning of the John Butters Power Station in 1993 and 1994 was approximately 5×10^6 m^3/day (Locher, 1997b, p. 13). The groundwater discharge from Bank D is therefore only a small fraction of the mean river flow (e.g., 0.004%). Even during minimum river flow (e.g., 5×10^4 m^3/day in 1994; Locher, 1997b, p. 19) it is still only 0.04 vol.% at the maximum estimated groundwater discharge rate of 18.77 m^3/day.

The groundwater velocity and residence time in Bank D are estimated by dividing the specific discharge, v, by the measured porosity. Assuming a typical porosity in Bank D of 0.45, groundwater velocity varies between approximately 0.4 m/yr (Series E in summer) and 25 m/yr (Series B in winter). The subsequent residence times for groundwater in the bank range from less than a year for the fastest velocities and narrowest part of the bank to approximately 26 years at the slowest velocities and widest parts of the bank. These estimates are based on hydraulic gradients calculated between piezometers and may represent only the approximate horizontal component of an overall hydraulic gradient. If the flow paths of groundwater were known, more accurate estimates of flow velocity and discharge could be calculated.

Ideally the full three-dimensional flow system in Bank D should be known, so that the flow paths would be accurately known. There are not enough data from the 33 piezometers to describe 3-dimensional flow, but the flow system could be calculated mathematically (e.g., by finite-difference or finite-element methods). At present it is not possible to calculate the flow systems accurately because of the heterogeneous nature of the sediment layers (e.g., organic-rich, highly permeable layers observed in trenches, layers and sections of different grainsize, porosity and hydraulic conductivity). In addition we do not know with certainty the locations and types of boundary conditions below the bank and between the bank and the valley side. Accurate calculations of total discharge are difficult because the cross-sectional area of discharge is unknown, the hydraulic gradients and hydraulic conductivity are variable throughout the bank and it is likely the groundwater flow is transient (because of changes in river level and flood and/or rainfall events).

In summary, the groundwater flow is variable throughout the bank. The estimated discharge of groundwater from Bank D is less than 0.05% of the river flow and up to two or three times higher in winter than in summer. By combining the geochemistry of the groundwater it is possible to calculate the mass loading of acid and elements to the King River from Bank D. The next section reviews the geochemistry of the groundwater and sediment, followed by calculations of the mass loadings and environmental impact of Bank D on the river water.

Groundwater geochemistry

The geochemistry of the groundwater in Bank D was measured to study its variability within the bank and between summer and winter seasons. The mineralogy and geochemistry of the sediment was identified and measured to understand more about the interactions between groundwater and sediment in Bank D.

The measured pH, Eh and major element concentrations in groundwater samples are presented in Tables 3 and 4. The temperature of groundwater was approximately 10°C during both field seasons. The pH was between 2.46 and 6.61 during the summer season and 2.44 and 6.02 in the winter season. In general, the groundwater was more acidic during winter, where the pH of samples taken from the same piezometers was up to 2 units lower than in summer, although the changes were variable and some waters were slightly less acidic in winter. The acidity of the groundwater increased towards the river. The average pH of summer samples was 4.5in piezometers nearest the river, 4.8 in the second row of piezometers and 5.5 in the third row of piezometers farthest from the river. The corresponding winter values were 4.0, 4.6 and 5.3. The pH also changed with depth; however, there are no clear trends. In some cases, pH increased with increasing depth and in others pH decreased with increasing depth. In one case, piezometers nearest the river in the E-series (Figure 2), the pH decreased and then increased with increasing depth. The variability reflects the transient nature of groundwater flow, heterogeneity of the bank sediments and possibly different bacterial species and populations.

The oxidation potential of the groundwater samples, measured as Eh, was also variable within the bank, with values ranging from approximately 55 mV to 680 mV. There are no clear trends in Eh; however, in general more reducing conditions (lower Eh) were encountered with increasing depth (e.g., >2m). In some cases, conditions were reducing enough to stabilise hydrogen sulphide (H_2S), which was detected by smell and gravimetric analyses of waters in some piezometers. The presence of hydrogen sulphide was probably because of bacterial activity (e.g., sulphate-reducing bacteria) and resulted in the precipitation of iron sulphide minerals (see below). Eh values in samples taken in winter were generally higher but this may have been due to lower pH values.

Major element concentrations were dominated by iron and sulphate in all groundwater samples, a result of the oxidation and dissolution of pyrite, e.g.,

$$FeS_2(s) + 7/2O_2(g) + H_2O = Fe^{2+} + HSO_4^{-} + H^{+}$$

Iron concentrations varied from several mg/l to greater than 2000 mg/l. No systematic trends were observed, where in some parts of the bank iron concentrations were higher in winter and in other parts they were lower. Sulphate concentrations varied from several tens of mg/l to greater than 5000 mg/l and as with iron there was no clear spatial or seasonal trends.

The concentrations of other major elements varied in differing amounts. Dissolved sodium and potassium were approximately constant in all samples and between seasons. Calcium, magnesium and manganese varied by approximately an order of magnitude and did not change systematically between seasons. Aluminum varied from below detection limit (0.1 mg/l) to greater than 100 mg/l, and had consistently higher concentrations during winter. Dissolved silicon varied less than an order of magnitude and had consistently lower concentrations in winter.

The variation in the concentrations of dissolved elements is a function of many possible geochemical variables, e.g., temperature, pH, Eh, ligand concentrations and processes, e.g., mineral solubility, adsorption and fluid mixing. Preliminary interpretations are presented below after a summary of the observed mineralogy and sediment geochemistry.

Many trace elements were detected in groundwater samples. Concentrations were variable and the elements reflect the nature of the mine tailings and the original ore material. Only a brief summary is given here - more complete details are available in Green (1997) and Green and McPhail (in preparation). In approximate order of decreasing concentration, the detected elements were Cu (0.001–350 mg/l), Co (0.009-2.3 mg/l), Zn (0.02-1 mg/l), Ba (17-77 µg/l), Ni (32-251µg/l), Pb (0.2-108 µg/l), Cr (0.07-15 µg/l), As (1-9.1 µg/l), U (0.1-8 µg/l), Cd (0.4-2.3 µg/l), Sn (0.01-0.15 µg/l) and in a few samples traces of Sb and Ti. During the summer season, only samples from piezometers in lines C, D, E and F were analysed for trace elements, whereas for the winter season data are available for all piezometers. In most cases where both summer and winter results are available, the dissolved trace element concentrations were higher in winter than summer, sometimes by nearly an order of magnitude (Green, 1997).

Sediment mineralogy and geochemistry

The sediment of Bank D is variable, where discontinuous layers are identified based on colour changes, amount of organic matter, hard-pan and mineralogy. The stratigraphy of Bank D is complicated and the thickness of individual sediment layers varies from 10-20 cm down to less than 1 cm. Mine tailings dominate the surface sediment as well as sediment samples taken during piezometer installation. In one piezometer, F7 (285cm deep), natural sediment was observed. That sample contained coarse (>2cm diameter), rounded sediment grains and no primary pyrite. It did, however, contain framboidal iron sulphide grains that probably resulted from biogeochemical reactions in the sediment bank (see below). In the top 30-100 cm the sediment is coloured red (i.e., oxidised), below which the sediment is grey (i.e., relatively unoxidised). The depth of oxidised sediment correlates approximately to the depth of the vadose zone, although the water table varies by tens of centimetres seasonally. Thin layers of relatively unoxidised tailings are present between oxidised layers in the shallower parts of the bank and, conversely, oxidised layers between relatively unoxidised layers in deeper parts of the bank. Some of the latter oxidised layers create a hard-pan, where quartz grains, lithic fragments, and perhaps significantly, slag grains (up to 30 vol. % of observed hard pan layers), are cemented together with iron oxyhydroxide precipitate. In addition, there are organic-rich layers that can be highly permeable and in some deeper parts of the bank contain framboidal sulphide grains.

The mineralogy of the sediment is dominated by quartz, although in oxidised zones at or near the surface of the bank many of the grains are coated by orange-red iron oxyhydroxide precipitate (e.g., goethite) that resulted from pyrite oxidation and dissolution. The coating is either amorphous or present in amounts too small to identify crystalline material unequivocally using conventional powder X-ray diffraction techniques. The following ranges of modal abundances were estimated based on petrographic analysis (Green, 1997). Quartz makes up 50-90 vol.% of the sediment and fine-grained clay (?) minerals make up 5-30 vol.%. The remaining non-opaque minerals consist of sericite + quartz lithic fragments (5-30 vol.%), muscovite (1-7 vol.%), chlorite (0.5-5 vol.%) and traces of other felsic and volcanic minerals. Organic matter (identified in hand specimen) content is variable and can represent as much as 10 vol.%. Sulphide minerals typically make up approximately 1 vol.% of the sediment. Pyrite predominates and there are lesser amounts of chalcopyrite, bornite, sphalerite and galena. Magnetite and hematite were identified in many samples, but in amounts much less than 1 vol.%. In deeper parts of the bank, framboidal iron sulphide can be up to 1 vol.% of the sediment. In more oxidised parts of the bank, typically at or near the surface, primary sulphide minerals (e.g., pyrite, chalcopyrite) were more prevalent (i.e., 1-10 vol. %) than in other parts of the bank.

The presence of framboidal iron sulphide grains may be significant in affecting acid generation and acid and metal transport, as the precipitation of iron sulphide could result in changes in acidity. For example, assuming hydrogen sulphide (detected in samples from deeper parts of the bank) and the initial precipitation of an iron monosulphide (observed in Bank D sediment; Wilkin and Barnes, 1996), the following reaction may generate increased acidity:

$$Fe^{2+} + H_2S(aq) = \text{“FeS” (s)} + 2H^{+}$$

The framboidal sulphide grains may also affect metal transport. Approximately 90 individual grains were handpicked from multiple sediment samples, dissolved and analysed for metal content (Green, 1997). The measured average metal concentrations were 1520 ppm cobalt, 760 ppm copper, 147 ppm zinc, 140 ppm lead and 120 ppm manganese. This may be important in trapping, or at least attenuating metals as they travel with groundwater through the sediment bank.

The geochemical composition of the sediment was measured in several ways. Samples and elements were selected based on locations in the bank (e.g., proximity to the river and depth) and the results of the measured groundwater compositions (i.e., samples where elements were in excess of recommended guidelines for water quality). Seven sediment samples (C1, D1, D3, E1, E2, F1 and G2) were digested in two ways: i) hot (85°C) nitric acid for three hours to determine “bulk” concentrations of selected elements (Fe, Mn, Al, Cu, Zn, Co and Pb) and ii) sequential extraction (e.g., Tessier et al., 1979) for the same elements to determine speciation of those elements in the sediment. The results are listed in Table 5. There are wide ranges in “bulk” concentrations and percentage fractions of the elements in different parts of the sediment and reflect the difficulty in obtaining accurate results and the heterogeneous nature of the sediment. Notably, large fractions of Mn, Zn, Co and Pb and in some cases Cu are in the “leachable” (i.e., extracted with $MgCl_2$) part of the sediment, indicating that these elements might be most easily leached from the sediment. The source of manganese and some of the iron is most likely the oxyhydroxide coatings on mineral grains, although carbonate minerals may also be an important source. The more dissolvable Al probably resides in fine-grained clay minerals (e.g., gibbsite, kaolinite and alunite). Cu, Zn, Co and Pb are most likely present as adsorbed species on, or coprecipitates with, the iron (and/or manganese) oxyhydroxide coatings on mineral grains, although Zn and Pb are also present in primary sulphide minerals. Slag particles may contain high concentrations of chalcophile elements (e.g., Cu, Pb, Zn, Co), as metal-containing sulphide droplets were observed in slag grains.

Geochemical Controls on Groundwater Geochemistry

Groundwater composition in Bank D is likely to be affected predominantly by water-sediment interaction because of the fine-grained sediment (i.e., high surface area) and redox reactions with sulphide minerals. In addition, acid generation probably requires interaction with the atmosphere and the framboidal sulphide grains are likely to be a result of bacterial activity. In order to understand more clearly what effects water-sediment interaction have on groundwater composition, aqueous speciation and mineral saturation indices were calculated using MINTEQA2 (Allison et al., 1991). The saturation index is the logarithm of the ion activity product divided by the solubility product for the relevant mineral (e.g., Drever, 1997, pp. 25 and 31):

$$S.I. = \log \frac{I.A.P.}{K_{sp}}$$

where the I.A.P. is a product of the calculated activities of ions in a mineral dissolution reaction and the K_{sp} is the equilibrium constant of the same reaction. The activities of the ions are calculated using measured water compositions (temperature, pH, Eh, element concentrations) and the computer program. The predicted saturation states of many minerals vary within only an order of magnitude; however, the saturation states of sulphide minerals are more variable than for other minerals and show trends with depth. Table 6 is a brief summary of the modelling results, where the listed minerals were either observed in the sediment, likely to be present in the fine-grained clay fraction or common in acid drainage environments. Only typical saturation indices are listed.

The minerals that are predicted to be supersaturated are mainly iron- and/or aluminum-bearing oxides, sulphates and silicates (Table 6), reflecting the high concentrations of Fe, Al and sulphate in the groundwater of Bank D (Tables 3 and 4). The concentrations of some dissolved elements, especially major elements, may be controlled by mineral solubility. Iron oxyhydroxide minerals (e.g., goethite and lepidrocite) may limit or control dissolved iron concentrations. The predicted saturation indices for crystalline goethite and lepidocrocite are approximately two log units supersaturated (Table 6); however, the coatings on mineral grains are probably amorphous (preliminary X-ray diffraction measurements; Green, 1997) and have a higher solubility than their crystalline counterparts. Their saturation indices would therefore be closer to zero. Dissolved silica is probably limited and/or controlled by SiO_2 minerals (e.g., quartz, amorphous silica) in a similar way as their saturation indices are close to zero (Table 6). Dissolved aluminum concentrations are close to being in equilibrium with some Al-bearing minerals (e.g., gibbsite and muscovite have saturation indices close to zero) but other Al-bearing minerals are supersaturated (e.g., alunite, pyrophyllite, jarosite and nontronite minerals), sometimes by greater than 15 orders of magnitude (Table 6). Controls on aluminum concentrations are complicated and it appears that the kinetics of precipitation reactions inhibit the precipitation of many of the possible aluminum minerals. Dissolved calcium and sulphate concentrations might be controlled by gypsum and/or barite solubility, although those minerals have not been observed in the samples from Bank D (barite has been observed in delta sediment; Hannan, 1996). Dissolved sulphate concentrations could be affected by other minerals (e.g., jarosite, alunite, Fe-sulphates, Fe-sulphides), but although some of these minerals are found in acid drainage environments, most have not been identified unequivocally in our studies. Trace elements, i.e., the heavy metals may be affected or controlled predominantly by adsorption (e.g., Drever, 1997, p. 196) or coprecipitation with iron oxyhydroxides and/or sulphides. Copper may be an exception where the saturation indices of chalcopyrite and chalcocite indicate those minerals are up to 11 orders of magnitude supersaturated.

There are many complicating factors that limit our present understanding of the sediment-water interaction in Bank D. Those factors include the heterogeneity in the sediment and groundwater mineralogy and compositions, uncertainties in the thermodynamic properties of minerals and aqueous species, the kinetics of dissolution and precipitation reactions, the effects of adsorption and the effects of elements and species that have not been considered in our studies yet (e.g., carbon), the effects of gas (e.g., CO_2, CH_4, H_2S) solubility in groundwater, and the effects of biological activity. In addition, the pathways that groundwater takes through the bank will affect how the groundwater and sediment compositions change. Chemical reactions (and water flow) in the unsaturated zone are obviously important as the degree of oxidation in the tailings is highest above the water table.

Environmental Impact of Sediment Banks along the King River

The environmental impact of sediment banks can be estimated by calculating the mass loading of elements to the river. The estimated discharge of groundwater (e.g., m^3/day) is multiplied by the concentration of dissolved elements in the groundwater. The effect of groundwater acidity on the river water is difficult to estimate accurately because measured pH values probably do not represent the total acidity of an acid-mine water. Following Taylor et al. (1996) the acid loading is calculated by using the measured pH and the measured iron (i.e., FeII) concentrations. The reason for including iron is because of the acid generation that could result from the oxidation of iron and precipitation of ferric iron minerals, e.g.,

$$Fe^{2+} + 5/2\ H_2O(l) + 1/2\ O_2(g) = Fe(OH)_3(s) + 2\ H^+$$

Mass loadings were calculated for each piezometer series and summed to estimate the total mass loading from Bank D. Acid loadings are calculated as sulphuric acid equivalent, and all loadings are calculated based on measured compositions of groundwater sampled in piezometers closest to the river. More complete water geochemistry was measured in the samples taken during the winter season (i.e., June 1997), so the following results are calculated for that time. The mass loading of the most important contaminants are 13 kg/day H_2SO_4-equivalent, 7kg/day Fe, 0.7 kg/day Al, 68 g/day Cu, 14 g/day Zn and 15 g/day Co. Mass loadings in the summer season (i.e., February 1997) would have been several times lower because the groundwater discharge was 2.4 times less and the pH and element concentrations approximately 20-50% lower in summer. The total estimated discharge to the King River from Bank D is small relative to the river flow (e.g., 0.04% calculated above), so the groundwater, and the dissolved acid and elements in it, will be diluted by approximately 2,500 times on entering the river.

Taylor et al. (1996) estimated the overall impact of the sediment banks and delta sediments on the water quality in the King River and Macquarie Harbour. They used a similar method as that outlined in this chapter, basing their calculations on results from 3 to 5 piezometers in each of four sediment banks (D, H, N and R; Figure 2) and 19 piezometers installed in the north and south lobes of the King River delta. They estimated a total discharge of groundwater into the river and harbour from 18 of the sediment banks (A – R; Figure 2) and the north and south lobes of the delta, assuming that the fluxes of groundwater to the river are the same in unstudied banks as they were in the 4 studied sediment banks. Their estimated total groundwater discharge was $2.3 \times 10^3\ m^3$/day, which represents 0.05 vol.% of the mean annual flow in the King River. They calculated mass loadings from groundwater, using their estimated discharge and measured groundwater chemistry and assuming that there is an equal contribution to mass loading from surface runoff. The sum of the two sources represents approximately 1 wt.% to 5 wt.% of the loading in the King River sourced upstream at the Mt. Lyell mine site at Queenstown (Taylor et al., 1996, p. 101). The contribution from mine tailings and slag particles in bottom sediments of the King River is unknown. They suggested that although the contribution from ground and surface water is small relative to the loads already in the river, acute events may have an adverse impact on the river water quality (e.g., flood, rainfall) by flushing higher concentrations of acid and elements out of the bank. In addition, their estimates are uncertain because of the variability of groundwater discharge and composition within sediment banks and in different seasons. The results of the subsequent studies summarised in this chapter show that the total groundwater discharge from a sediment bank can vary by several times between summer and winter and the groundwater composition can vary by orders of magnitude within the bank and by several times between summer and winter.

The mine tailings in the river system are likely to contaminate the river and harbour water for a long time. Contamination may continue for approximately 2000 years, based on an approximate pyrite concentration of 2 wt.%, a copper concentration of 0.085 wt.%, an estimated 2.73 million tonnes of tailings in the sediment banks and delta and an acid-producing potential from pyrite of 33 kg H_2SO_4-equivalent/tonne and current groundwater discharge rates (Taylor et al., 1996, p. 101). This estimate is uncertain because the transient effects of climate, groundwater flow and discharge, river flow and the geochemistry of the contaminated sediment. In addition, some banks show some signs of revegetation and there has been limited success in revegetation trials, both of which may reduce the generation of acid and mass loadings of acid and toxic elements to the river system.

Summary and Conclusions

The hydrogeology and geochemistry of sediment banks on the King River, Tasmania have been studied in order to estimate the impact of mine tailings on the water quality in the King River and Macquarie Harbour. Hydrogeological studies allow the estimation of groundwater discharge into the river. By combining with measured groundwater geochemistry, mass loadings of acid and elements to the river system have been estimated. Geochemical studies of the groundwater and sediment within the bank also help in understanding water-sediment interaction, including acid generation and element leaching, transport and deposition. One particular sediment bank (Bank D) approximately 2.5 km upstream of the King River mouth has been studied in detail to gain an understanding of spatial and seasonal variability in groundwater flow and geochemistry and the interaction between sediment, atmosphere and water and the controls on groundwater composition in the bank. Several other banks and the delta were studied in similar way but in less detail. The significant outcomes of these studies are:

- Groundwater flow in Bank D is mainly perpendicular towards the river; however, some of the upstream end of the bank, particularly in summer, has flow into the bank from the river. Water levels, hydraulic gradients and groundwater flow are greater in winter.

- Estimated residence times for groundwater in Bank D vary from less than a year to approximately 14 years, although flow in some parts of the bank be higher and residence times lower because of observed highly permeable and discontinuous sediment layers.

- Total discharge of groundwater into the King River from Bank D is estimated to have been approximately 8 m^3/day during summer (February, 1997) and 19 m^3/day during winter (June, 1997). The highest discharge probably represents at most 0.04 vol.% of the mean annual river flow in the King River.

- The geochemistry of the groundwater in Bank D was highly variable. Groundwater was acidic ($2.4 < pH < 6.6$) and increased in acidity closer to the river. The pH was up to two units more acidic during the winter. Groundwater and sediment were oxidised near the surface (e.g., approximately the top 10 cm to 50 cm) and in some parts of the bank reducing conditions (i.e., presence of hydrogen sulphide and biogenic sulphide grains) were encountered at depths greater than approximately 2 metres. Element concentrations were dominated by ferrous iron and sulphate, mainly due to the oxidation and dissolution of pyrite present in the mine tailings. Most major element concentrations by up to an order of magnitude and there was no systematic change between summer and winter. Aluminum concentrations were higher in winter than summer and silicon concentrations were lower in winter. Trace element concentrations varied by several orders of magnitude and were generally higher in winter than in summer.

- Sediment consists of fine-grained mine tailings, natural sediment and organic matter. The mineralogy of the sediment is dominated by quartz, with lesser amounts of lithic fragments, muscovite, chlorite, iron oxides and sulphide minerals (pyrite, chalcopyrite, bornite, sphalerite and galena). Framboidal sulphide (biogenic) grains were present in deeper parts of the bank.

- Some dissolved element concentrations, e.g., Si, Fe, Ca, SO_4^{2-} and possibly Al and Cu, appear to be controlled by mineral solubility. Other elements may be controlled by adsorption and/or coprecipitation with iron oxyhydroxide coatings and framboidal iron sulphide minerals.

- The impact of the groundwater discharge on present-day water quality in the King River and Macquarie Harbour is small – most of the acid and metal load in the river is sourced from the Mt. Lyell mine site. The estimated groundwater discharge from all sediment banks and delta sediments is only 0.05 vol.% of the river flow. The groundwater is contaminated with acid and potentially toxic elements, but the estimated mass loadings are on the order of 1 wt.% to 5 wt.% of the load in the river.

- There appears to be a natural attenuation process for metal transport in Bank D, where the precipitation of iron sulphide minerals, presumably resulting from bacterial sulphate reduction, traps heavy metals in deeper parts of the bank.

It is difficult to estimate accurately the magnitude of environmental impact of contaminated sediment banks on river water quality. The heterogeneous nature of riverbanks and the transient flow makes it difficult to estimate flow velocity and discharge accurately. The geochemistry of sediment is also heterogeneous, especially because of the variation in oxidation potential (e.g., oxidised at surface, reducing at depth). Although the sediment geochemistry may not vary as much in time, the groundwater geochemistry varies in both space and time, where depending on the element, their concentrations can be higher or lower in different seasons. The mass loading of acid and contaminants from a sediment bank into a river could be estimated by measuring water chemistry above and below the bank, but differences would probably be undetectable in cases like the King River, where the river flow is orders of magnitude higher than discharge rates from the bank. Finally, the environmental impact of sediment banks on river quality may not result entirely from groundwater discharge. Overland flow or aeolian transport may also carry contaminants into the river.

Future research into problems should include sampling more often to understand the transient nature of groundwater flow and composition. The water flow and geochemistry in the unsaturated zone should be studied. Reactive transport modelling of sediment-water interaction will provide insight into how groundwater compositions change along the flow path through contaminated sediment. Measuring and studying organic carbon compounds (solid and aqueous) and bacteria in sediment banks is also necessary for a complete understanding of the geochemical evolution of the sediment and groundwater.

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Figure Captions

Figure 1. Location map for the catchment of the King River, Tasmania. For reference, Queenstown is shown in both inset and main map. Catchment is shown in white. Major roadways are shown in dark grey lines and labelled with letters and numbers, e.g., A10. White lines are the boundaries of World Heritage Areas. Modified from Taylor et al. (1996).

Figure 2. Location map for sediment banks on the King River, Tasmania. Banks are shown as stippled areas and labelled with letters. Dashed lines represent roads or tracks. King River catchment is shown in white. Modified from Taylor et al. (1996).

Figure 3. Bank D of the King River, Tasmania. Piezometer locations are marked with symbols and labelled with letter and number. Piezometer nests are labelled with more than one number, e.g., C2/3. Solid lines in the western part of the bank are ephemeral streams. WREB stands for West River East Bank and EREB, ERWB stand for East River East and East River West Bank, respectively. Lightly shaded areas north of the road and south of the King River are valley sides.

Figure 4. Hydraulic head contours in summer and winter for Bank D of the King River, Tasmania. Contours are in 10cm intervals relative to the average river level during times of hydraulic head measurement. The locations of piezometers used to calculate contours are marked with symbol and labelled with letter and number. Lightly shaded areas to the north of the road and south of the river are valley sides.

Table 1. Depths of piezometers installed in Bank D of the King River, Tasmania (Hooper, 1997). Locations of piezometers are shown in Figure 3. Ground elevation is relative to the average river level in February and June 1997.

Piezometer	Ground elevation (cm)	Depth (cm)
A1	111.0	213.7
B1	144.1	204.8
C1	128.6	168.8
C2	148.9	234.4
C3	145.1	279.7
D1	86.4	242.9
D2	126.5	161.3
D3	128.0	92.0
E1	114.2	259.7
E2	132.2	121.2
E3	144.6	145.9
E4	127.7	272.7
E5	121.7	341.0
F1	105.2	206.7
F2	131.2	124.0
F3	107.4	87.4
F4	113.9	325.7
F5	105.0	225.9
F6	114.8	355.0
F7	133.1	285.0
G1	67.5	228.1
G2	134.3	212.1
G3	164.3	122.4
G4	170.9	366.1
H1	82.2	212.2
H2	128.9	118.4
H3	96.1	236.4
I1	99.6	125.9
WREB1	150.6	238.0
WREB2	149.7	117.3
WREB3	106.3	220.1
EREB	140.0	255.3
ERWB	127.0	266.3

Table 2. Calculated groundwater discharge from Bank D into the King River, Tasmania.

Piezometer Series	Section Width[1,2] (m)	Hydraulic Conductivity[2] (m/s)	Hydraulic Gradient[2] (m/m)		Discharge (m^3/day)	
			Summer[3]	Winter[3]	Summer	Winter
A	109	8.52×10^{-7}	0.0134	0.0602	0.43	1.93
B	40	9.56×10^{-6}	0.0137	0.0381	1.81	5.04
C	55	8.55×10^{-6}	0.0124	0.0300	2.02	4.88
D	85	2.42×10^{-6}	0.0074	0.0154	0.53	1.09
E	90	4.93×10^{-7}	0.0125	0.0237	0.19	0.36
F	105	2.29×10^{-6}	0.0207	0.0481	1.72	4.00
G	110	7.94×10^{-7}	0.0087	0.0185	0.26	0.56
H	95	6.07×10^{-7}	0.0184	0.0208	0.37	0.41
I	145	3.06×10^{-7}	0.0221	0.0326	0.34	0.50
				TOTAL	7.67	18.77

[1] Depth of cross-sectional area of groundwater flow is assumed to be 4 m.

[2] Section widths, hydraulic conductivities and hydraulic conductivities are from Hooper (1997)

[3] Summer refers to February 1997 and Winter refers to June 1997

Table 5. Ranges of selected element concentrations and percentages of those elements in different sediment fractions in sediment samples from Bank D of the King River (Green, 1997). The ranges are for seven samples (piezometers C1, D1, D3, E1, E2, F1 and G2; Figure 3). Details of the analytical techniques are given in the methods section of text.

Element	"Bulk" (ppm)	Exchangeable (wt. %)	Acid Soluble (wt. %)	Reduceable (wt. %)	Oxidisable (wt. %)	Immobile (wt. %)
Fe	430-29,000	1-6	0-4	11-31	2-37	41-79
Mn	1-247	38-62	1-9	0-8	0-15	19-60
Al	306-11,000	2-5	0-3	4-16	6-20	54-83
Cu	25-437	2-49	5-25	0-16	6-76	5-36
Zn	7-118	16-70	0-7	0-16	0-9	27-72
Co	3-49	73-100	0	0-7	0-13	0-14
Pb	8-74	0-100	0-12	0-20	0	0-83

Table 6. Typical calculated saturation indices of some minerals in groundwater samples of Bank D of the King River (Green, 1997).

Mineral	Saturation Index	Notes
SUPERSATURATED MINERALS		
Nontronite (Na, K, Mg, Ca)	9 – 16	Possible clay minerals
Hematite	9	Observed
Magnetite	7	Observed
Jarosite (Na, K)	4 - 7	Likely in oxidised zones
Kaolinite	3	Possible clay mineral
Pyrophyllite	5.5	Possible clay mineral
Alunite	5	Likely in oxidised zones
Montmorillonite	3	Possible clay mineral
Lepidocrocite	2.1	Possible iron oxyhydroxide mineral
Goethite	1.9	Probable iron oxyhydroxide mineral (observed?)
Muscovite	1.2	Observed (muscovite, sericite)
Diaspore	1.2	Possible clay mineral
Quartz	1.1	Observed
SATURATED MINERALS		
Barite	0.8	Possible sulphate mineral
Cristobalite	0.6	Potential fine-grained mineral
Chalcedony	0.4	Potential fine-grained mineral
Halloysite	0.2	Potential fine-grained mineral
Gypsum	-0.1	Possible/likely
SiO_2 (amorphous)	-0.4	Probably part of fine-grained material
Leonhardite	-0.5	Potential fine-grained mineral
Gibbsite	-1	Potential Aluminum clay mineral
SULPHIDE MINERALS		
Pyrite (vadose zone)	-10	Observed
Pyrite (saturated zone)	3-20	Observed (primary, secondary)
Greigite	-0.5 to - 2	Possible in framboidal sulphide
Chalcopyrite (saturated zone)	11	Observed
Covellite (saturated zone)	8	Possible copper sulphide
Galena	-0.8 to -1.2	Observed
Sphalerite	-3	Observed
CoS	-5	Possible in framboidal sulphide
MnS	-12	Possible in framboidal sulphide