Bioaccessibility of metals in sediments and soils impacted by acid mine drainage in mount morgan (Queensland, Australia)

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Abstract
Acid mine drainage (AMD) into the Dee River from the historic gold and copper mine in Mount Morgan, Queensland (Australia) is a continuing problem. The pH of the river water is consistently below 3.5 for 18 km downstream of the mine site to its junction with the unimpacted Fletcher Creek. Metal levels in the river water adjacent to the mine were generally elevated (e.g. Al 191 mg/L, Cd 0.06 mg/L, Cu 16.7 mg/L, Pb 0.10 mg/L and Zn 6.4 mg/L). Sediments downstream of the mine site contained elevated Cd, Zn and especially Cu (up to 1700 mg/kg). Soils on the Dee River floodplain (60 km downstream of the mine) were also contaminated with Cu (up to 2510 mg/kg). The bioaccesibility (or potential bioavailability) of metals in sediments (sampled during low and high flows) and in soils were assessed using the BCR sequential extraction (into four fractions) scheme. The fractionation scheme provides a helpful tool in environmental risk assessment by predicting metal contaminant availability. More than 50% of Cu, Cd, Mn and Zn in sediments and soils were associated with the two most mobile fractions (acid-soluble, F1 and reducible, F2), with metal concentrations in these fractions alone mostly exceeding the Australian sediment or/soil quality guidelines. Analyses of lucerne and mandarin oranges grown in the area showed no significant metal contamination. Cu and Zn plant contents in pasture grass in the AMD-contaminated floodplain showed good correlation (0.81 and 0.70, respectively) with their respective soil contents, consistent with predicted bioaccessibility (approximately 60% for F1+F2) of the soil-bound metals. More studies are needed to confirm bioaccessibility of Cd, Mn and Pb, which showed high F1+F2+ reducible fraction, F3.

Introduction
The historic gold and copper mine at Mount Morgan in central Queensland commenced in 1882 and ended in 1981, although re-treatment of the tailings to recover gold continued until 1990. It is well-known for its continuing acid mine drainage (AMD) problem. Community complaints of acid pollution in the river date back to at least 1925. Some areas in the lower Dee River catchment are used extensively for the forage crop lucerne, while the floodplain land is used exclusively for grazing beef cattle on pasture grass.
The Wowan Dululu Landcare Group Dee River Sub Committee was formed to raise awareness of the AMD problem and to coordinate the Dee River Research Project, which included this study. This paper is limited only to the assessment of the bioaccessibility (or potential bioavailability) of the metal contaminants in sediments and soils. Agricultural produce (used for cattle or human consumption) were studied to determine any impacts of AMD.
Studies of metal speciation are considered to be more meaningful in assessing the potential risk from sediment- or soil-bound metals on aquatic/terrestrial biota than simply measuring total metal concentration (Tessier *et al*. 1979; ANZECC 2000). The modified BCR sequential extraction scheme (Rauret et al., 1999) was applied to sediments and soils in this study. The scheme fractionates metals into four fractions (in decreasing ease of remobilisability): acid-soluble (F1), reducible (F2), oxidisable (F3) and residual (F4) components. The sum of these four fractions is approximately equal to the total metal concentration. Metals in F1, F2 and F3 are labile and reactive and viewed to be potentially bioavailable, with metals in F1 being most mobile when waters are acidic; metals in F4 have little potential bioavailability (Tessier et al. 1979).

Materials and Methods
The study included a reference site 4.5km upstream of the mine, the mine site and 16 sites up to 83 km downstream from the mine site. Surficial sediments (0-5 cm during low flow; 0-2cm during high flow) were collected from six sites during low flow (Dec1999-Aug2000) and high flow (Nov2000-Jan 2001) periods. Sediment cores (12-30cm depths) were taken from three locations: upstream, 47 km and 83 km downstream of the minesite . All sediments/soils were dry-sieved through nylon sieves; sediment particles <60μm and soil particles <2 mm were used for analyses.
Five fields along the Dee River were sampled for lucerne and two fields at the Dee River floodplain for pasture grass. A citrus (mandarin trees) orchard located adjacent to the Dee River at Dululu was also sampled. Reference fields included two lucerne fields and two pasture fields from the Don River Catchment, upstream of its junction with the Dee River. A reference citrus orchard was chosen at Emerald (Central Queensland) which had similar soil type (sandy loam) and irrigation practices (using river water). There were no known sources of AMD in both the Don River or Emerald reference sites.
Metals and S were analysed by ICP-OES, except for Cd and Pb which were determined by ICP-MS.

Results

Table 1 shows the metal concentrations of sediments from some of the study sites, as well as the ANZECC (2000) guidelines for bulk sediments and the 'pseudo' trigger levels which have been derived for <60µm fraction. The upper 12 cm of sediment cores obtained downstream of the mine confirmed significant Cu, Zn, Cd and S contamination.

Table 1. Metal concentrations Dee River sediments pre- and post- acid flows.

Site	Concentration (mg/kg dry wt)			
(km from mine)	Cd	Cu	Pb	Zn
Pre Acid Flow (Dec 1999/Aug 2000)				
Site 5 (22km)	4.8	2,631	30	602
Site 7B (47km)	2.9	899	13	436
Site 8A (60km)	0.6	294	12	159
Post Acid Flow (Jan 2001)				
Site 5 (22km)	2.6	1,835	12	756
Site 7B (47km)	1.9	446	11	275
Site 8A (60km)	1.5	689	17	295
ANZECC (bulk)	1.5	65	50	200
Pseudo (< 60µm)	0.6	390	60	300

Figure 1 shows the average concentration of each metal in sediment fractions F1 to F4.

Table 2 gives the mean total concentrations of floodplain soils, clearly indicating Cu, S and Zn contamination. The soils exhibited very similar fractionation behavior as the sediments. Cd, Cu, Mn and Zn in F1, F2 or F3 exceeded the interim ecological investigation levels, EIL (NEPC 1999).

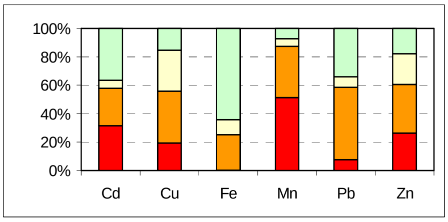

Figure 1. Average (n = 6) distribution of metals in the four fractions (bottom to top = F1 to F4), expressed as a percentage of the total concentration for sediment samples collected pre- and post- flow in the Dee River.

Only a limited number of plant/agricultural samples were analysed, The concentrations of metals in lucerne and lucerne hay were found suitable for cattle dietary intake. Cd, Cu, Pb and Zn levels in citrus (mandarin) samples were below the maximum allowable concentrations in the Australian food code (ANZFA 2001). Cu and Zn in the floodplain pasture grass correlated (0.81 and 0.70, respectively) with the respective metal soil contents, consistent with predicted bioaccessibility (approximately 60% for F1+F2) of the soil-bound metals.

Table 2. Mean metal concentrations (n = 4) in pasture soil from the Dee and Don River floodplain.

	Mean Concentration (mg/kg dry weight)			
	Cu	Fe	S	Zn
Ref P1 (Don River, upstream of Dee junction)	66	50,200	311	102
Dee P1	671	73,200	685	153
Dee P2	2,080	83,000	1,126	573
NEPC (EIL)	100	-	600	200

Discussion

Surface sediments and soils, particularly at the Dee River floodplain showed significant AMD contamination. These metals in sediments or soils could have been released to the water column during the 2000/2001 high flows when the Dee River water pH was < 5 for a distance up to 60 km. From Figure 1, more than 50% of Cu, Cd, Pb, Mn and Zn were associated with the most mobile sediment fractions (F1 and F2), which had concentrations that mostly exceeded the ANZECC (2000) sediment quality guidelines and are potentially bioaccessible. The fractionation scheme could be refined to provide a helpful tool in assessing potential risk or predicting bioaccesibility of contaminant metals in sediment or soils before conducting any plant/animal analyses.

Although the metal contents in the plants were within acceptable levels, the practice of river water irrigation of the lucerne fields and citrus orchards need to be monitored regularly for any AMD impacts on these agricultural produce. Beef cattle can ingest some of the contaminated pasture soil or sediment on the floodplain and are potentially vulnerable.

Acknowledgements

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