Development of site specific guidelines for future land use at the Woodcutters lead zinc mine

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Abstract
The National Environment Protection Measures (NEPMs) guidelines for soil contamination in Australia require further assessment if the Health Investigation Levels (HIL) are exceeded. It was identified that the current NEPM's do not provide accurate close out criteria for mined land as the bioavailability of contaminated soil is usually a fraction of 100%. Absolute bioavailability is measured via animal uptake but is expensive and time consuming. A more practical approach uses in-vitro PBET (physiologically based extraction test) to determine the bio-accessibility of individual soils. A risk assessment conducted on a metal and metalloid survey of surface soils representing different categories of mine wastes employed as risk assessment tools: (i) in-vivo bioavailability measurement of composite wastes using rats; and (ii) the in-vitro PBET (physiologically based extraction test) determination of bio-accessibility of individual soils. All mine waste samples were tested for bioaccessibility (PBET) under various pHs in a synthetic gastric fluid system. pH values were 1.3, 2.5 and 4.0 simulating fasting, partially fed and fed stomach conditions respectively, and at pH 7.0 simulating the small intestinal pH condition. The bioavailability of arsenic was 1.6 – 8.9% but arsenic bioavailability is dependent on its oxidation states. Arsenate (AsV), the oxidized form of arsenic, is more likely to be found in mine waste materials. Arsenate bioavailability from these mining wastes was found to be <5% whereas arsenite (AsIII) could be as high as 8.9%. Conservatively, 10% bioavailability for arsenic could be used for exposure assessment. The bioavailability of lead was 0.6 – 1.4%. Similarly, bioavailability of 2% was used for risk assessment purposes. In-vitro bioaccessibility screening level using the PBET method was the more conservative approach. Based on the risk assessment approach that was used site specific health investigation levels for arsenic and lead could be proposed that may be adopted for mined land and enable future land uses to be determined.

Key Words
Lead, arsenic, mining, soil, site-specific guidelines.

Introduction

Developing closure criteria for Woodcutters Mine in Northern Australia has involved multiple investigations to support site specific thresholds for a number of key indicators including available metals concentrations in soils. In Australia "Enduring Value" of the Mineral Council of Australia promotes the need to have rigorous mine closure programs well in advance of mining completion and identifies the need to have quantitative indicators of rehabilitation success.

Base metal mining is accompanied with requirements to ensure that effects of heavy metals and metalloids do not impact on human health and the environment as part of the closure process. Australia has national guidelines for soil called National Environment Protection Measures (NEPMs) (NEPC 1999) to give an indicative protective measure of from contamination of heavy metals and metalloids. When the designated soil guidelines are exceeded, a Tier 2 health risk (or ecological risk) study is required to measure bioavailability and determine the % total concentration that is available to human or other biota uptake. Bioavailability (BA) is measured by animal uptake experiments using rats but is an expensive process. An alternative is to measure the bioaccessibility (BAc) using a physiologically-based extraction test or PBET (Bruce *et al.* 2007). Rat bioavailability is used to calibrate and confirm the wider use of the PBET method.

The Woodcutters soil anomaly was discovered in 1966 and mining commenced in 1984. The Woodcutters Mine was operational from 1985 until March 1999, producing 539,000 tonnes of zinc; 245,000 tonnes of lead; 16 million ounces of silver for export; and 3,650,000 tonnes of ore. Ore production commenced from

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the open pit in 1985 and became an underground operation in 1986. Mining ceased in March 1999 when economic ore was depleted. Newmont Asia Pacific took over the Woodcutters site in February 2002 and have progressed the mine closure program for the site.

This study seeks to: (i) Identify key hazards to map extent of contamination from mining; (ii) Undertake studies of PBET to map contamination; (iii) Confirm reliability of bioaccessibility through bioavailability measurement (rats): (iv) Establish site specific guidelines based on bioaccessibility and bioavailability assessments; and (iv) Undertake further remedial works and confirm if mine closure is satisfactory.

Methods

A risk assessment was conducted based on a metal and metalloid survey of 60 surface soils representing 4 categories of wastes. In a soil survey conducted in September 2005, 60 soil samples representing 4 different categories of mine waste materials encompassing tailings, waste rock, processed material and contaminated ground. The soils were ground finely, digested in aqua regia and the concentration of each element determined by ICP-AES. Mean concentration data of various arsenic and metals in categories of mine wastes is summarised in Table 1.

Table 1. Concentrations (mean ± s.e.) of arsenic and metals in 4 categories of mine waste materials

Element (mg/kg)	Category 1	Category 2	Category 3	Category 4
Arsenic	180±50	1340±720	330±40	450±50
Cadmium	120±70	70±40	9±3	5±1
Cobalt	44±9	23±2	27±2	37±3
Copper	105±10	130±30	120±30	110±8
Nickel	120±16	52±8	65±8	110±9
Lead	840±280	5450±2700	870±230	550±80
Zinc	7800±2400	7700±4400	1200±470	820±120

Two different approaches were employed as the risk assessment tools: (i) in-vivo bioavailability measurement of composite wastes using rats; and (ii) the in-vitro PBET (physiologically based extraction test) determination of bioaccessibility of individual soils. All mine waste samples were tested for bioaccessibility (PBET) under various pH values in a synthetic gastric fluid system. pH values for the extraction tests were 1.3, 2.5 and 4.0 simulating fasting, partially fed and fed stomach conditions respectively, and at pH 7.0 simulating the small intestinal pH condition.

A desk top risk assessment was prepared focusing on metal concentrations which are higher than current health guideline values. In the absence of site specific bioavailability and exposure data, a worst case scenario initially is necessary to identify potential "hot spots" based on an accepted risk assessment framework (enHealth 2004).

In-vivo bioavailability test – rat study

The mine materials of each area were used to make a composite of equal amount of each element. Rats weighted at approximately 180 g each were divided into groups each of 4 rats. For positive controls, rats were injected intravenously using the salt solution and the other groups were given slurry of mine material by oral gavage. The mine materials were weighted for each rat separately according to the dose rate and body weight. The rats were kept in individual metabolic cages and were fasted over the night before the dosing day. The dose rates were: arsenic 0.5 mg/kg (in the form of sodium arsenate or sodium arsenite); and lead 0.01 to 2.7 mg/kg (lead acetate) dependent on waste concentration. Urine samples were collected 24 h prior to dosing and then daily over 10 days post dosing.

In-vitro bioaccessibility test – PBET

All mine waste samples were tested for solubilised fraction (bioaccessibility) under various pH values in a synthetic gastric fluid system (PBET – physiologically based extraction test). Mean percentages of bioaccessibility for arsenic, cadmium, cobalt, copper, nickel, lead and zinc from 4 categories of waste materials are shown in Table 2.

Results

Historical investigations into the distribution and concentrations of metals at the Woodcutters mine site indicate that there was an elevated natural background of various minerals. Accordingly, in 2006 site specific

remediation guidelines were developed by EnTox following bioaccessibility studies. The approach adopted follows the procedure established by the NEPC (1999) and led to the further refinement of the proposed remediation guidelines (Table 2). The measure of % BAc using PBET and confirmed by rat bioavailability (%BA) on key soil types enable the development of site specific remediation guidelines and indicated that the extent of contamination was limited to a number of small discrete locations.

Table 2. Summary of guidelines for Woodcutters mine site remediation

Metal/metalloid	% BAc 2005	% BA 2005	%BAc 2006	NEPM Level E	EnTox 2006 Remediation Guideline
Arsenic	3-10	1.6-8.9	2-22	200	1000
Cadmium	17-30	-	1-46	40	80
Cobalt	6-18	-	6-18	200	1,000
Copper	5-13	-	4-22	2000	10,000
Lead	10-18	0.6-1.4	11-38	600	1,500
Nickel	4-17	-	4-17	200	2,000
Zinc	23-27	-	10-36	14,000	40,000

Although the EnTox 2005 soil survey results for total Pb and As were relatively high in the rehabilitated areas, the results for % BAc indicated that the contamination was not a significant health risk (Table 1). Only Cd at one site and Pb at 4 sites were considered to be contaminated and significant compared to the EnTox 2006 remediation criteria.

Conclusion

The investigation and development of site specific thresholds demonstrates that careful examination of specific source characteristics and receiving context can greatly improve the focusing and application of resources in closure processes. This had a significant bearing on the focus and extent of remediation activities and success of this mine closure process.

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