Study of Heavy Metals and Metalloids in the Leichhardt River and Surrounding Locations

Lead Pathways Study - Phase 1 (Emissions to Land)



Report by:

Barry N. Noller Centre for Mined Land Rehabilitation

Vitukawalu P. Matanitobua and Jack C. Ng National Research Centre for Environmental Toxicology

THE UNIVERSITY OF QUEENSLAND

Prepared for:

Mount Isa Mines Limited Private Mail Bag 6 Mount Isa

26 June 2009











This report was prepared by the Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, Queensland 4072.

The report was independently reviewed by an environmental soil contamination specialist, Professor Michael J. McLaughlin.

Professor Michael J. McLaughlin, B.Sc. (Hons), M.Agr.Sc. (Dist.), Ph.D.

Chief Research Scientist and Director of CSIRO Centre for Environmental Contaminants Research, CSIRO Land and Water and Professor in the School of Earth and Environmental Sciences, The University of Adelaide

Professor McLaughlin is a foundation Director of CSIRO's Centre for Environmental Contaminants Research and also a Professor in the School of Earth and Environmental Sciences at The University of Adelaide. He sits on the Queensland Water Commission Expert Advisory Panel on water recycling, and on the international metals industries' Ecotoxicity Technical Advisory Panel.

Professor McLaughlin received his BSc in 1977 (Univ. Ulster), MAgrSc in 1979 (Reading Univ.) and PhD in 1986 (Univ. Adelaide). Before joining CSIRO Land and Water in 1991, he worked as a research scientist at the Soil and Irrigation Research Institute in South Africa dealing with sustainability issues relating to wastewater and sewage biosolid disposal on soils, particularly with concerns relating to metals and phosphorus. Professor McLaughlin also worked in CSIRO Plant Industry in Canberra on issues relating to acidic soils and reactions of fertiliser phosphorus and fluoride in soils. From 1988 to 1991 he was Technical Manager of the Australian Phosphate Corporation and Honorary Research Fellow at La Trobe University, Melbourne, responsible for environmental issues relating to fertiliser use in Australia.

Professor McLaughlin's entire research career has focussed on the impacts and chemistry of nutrients and contaminants in soil and food quality, agricultural re-use of wastewaters and solids, and environmental risk assessment, specifically the assessment and remediation of contaminated soils, and the behaviour and toxicity of contaminants in the soil system. He is a prolific producer of research outputs with more than 191 referred publications and numerous books, book chapters, conference papers and industry publications to date.

Copies of this report may be obtained by contacting: Xstrata Mount Isa Mines community information line on 1800 336 297

Executive Summary

This report describes a study of heavy metal and metalloid contamination of the Leichhardt River and the swimming pool/ Kruttschnitt oval area at Mount Isa, undertaken to assess the significance of residual contamination from mine sediments largely resulting from mine practices in the 1940s.

The study used targeted sampling at 21 locations to:

- (i) Determine the distribution of contamination within an area known to be previously contaminated;
- (ii) Calculate the bioaccessible¹ (BAc) fraction of total heavy metals and arsenic using a PBET method (physiologically-based extraction test);
- (iii) Complete a desktop human health risk assessment using bioaccessibility as a surrogate for bioavailability² to estimate the site-specific potential toxicity of lead and arsenic; and
- (iv) Compare sediment concentrations with Australian and New Zealand Environmental Conservation Council (ANZECC 2000) Interim Sediment Quality Guidelines (ISQG) as a measure of potential ecological toxicity.

The first step in the human health risk assessment for soils in the Leichhardt River was to compare the total concentrations of heavy metals and arsenic against the National Environmental Protection Measure (NEPM) Health Investigation Level (HIL) Level E (NEPC, 1999). The Level E Health Investigation Level applies to parks, recreational open space and playing fields. Residential sites were not a part of this study. This comparison of concentrations in soil assumes 100% bioavailability and initially showed that exceedances occurred at a number of sites for arsenic, cadmium, cobalt, copper, lead and zinc. Sites at the swimming pool and the Leichhardt River downstream were below the HIL Level E concentration and did not show evidence of contamination.

According to the National Environmental Protection Council (NEPC) risk assessment process, exceedances of the HILs trigger the requirement to undertake a Tier II risk assessment including toxicity assessment. Hence

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

¹ Bioaccessibility (BAc *in-vitro*) is the fraction of the total concentration that has the potential to be absorbed into the human body as estimated by simulation of the gastro-intestinal tract (see Glossary for complete definition).

² Bioavailability (BA *in-vivo*) is the amount of a contaminant that is absorbed into the body following skin contact, ingestion, or inhalation (see Glossary for complete definition).

bioaccessibility, used to predict bioavailability, was calculated for each of the sites to allow for site specific risk assessment.

The values of the key contaminants were adjusted for bioaccessibility and compared, once again, with the NEPM HIL Level E criteria. After bioaccessibility was taken into account fewer metals/metalloids were of concern and the number of sites considered to be contaminated with respect to human health was reduced.

The area of known contamination, in the river between Grace Street Bridge and downstream of the Velodrome continued to show exceedances of the NEPM HIL Level E criteria for lead, copper, cadmium and zinc. Copper was also still in exceedance of the criteria at the Death Adder Gully sites.

The significance of lead and arsenic in soil to human health was assessed by conducting a desktop human health risk assessment that examined both acute and chronic effects. It determined that:

- Contaminated soils, as sampled in this study, are unlikely to cause acute or sub chronic lead or arsenic toxicity;
- Chronic lead toxicity is unlikely to occur in adults;
- In a residential scenario, elevated concentrations of lead in soil combined with high bioavailability (i.e. soils with concentrations of >1,200 mg/kg with a bioavailability of >20% or concentrations >2,400 mg/kg with bioavailability of >10%) do have the potential to cause chronic lead toxicity in children. It must be noted that related studies have shown that lead bioavailability is generally much lower than bioaccessibility as used to predict bioavailability in this study. Risk is reduced even further in recreational areas as the exposure time is greatly decreased; and
- Arsenic in soil is unlikely to cause chronic toxicity in humans because people are not likely to ingest sufficient amounts of soil under normal circumstances.

The ecological risk assessment of sediments in the Leichhardt River involved comparison of the concentrations of heavy metals and arsenic with the ANZECC (2000) sediment guidelines (ISQGs). Results of the ecological risk assessment indicated that all sites including the background site exceeded one or both the ISQG–High and ISQG–Low trigger values based on total concentrations. A lesser number of sites exceeded the ISQG-Low trigger values once the 1M hydrochloric acid extract was used as an indication of bioavailability.

To assess the significance of the exceedances of the ANZECC ISQG trigger levels, an ecological toxicity assessment was undertaken using aquatic macroinvertebrate species. The test results indicate that only the zone of sediment in the Leichhardt River adjacent to the Velodrome has potential to be toxic to aquatic biota and requires further assessment. However, all sites where sediments exceeded the ANZECC ISQG-Low trigger may require further ecological risk assessment by using a more comprehensive suite of test organisms.

The likelihood of future acidification of rock material causing release of heavy metals was found to be low.

The findings presented in this study resulted in further remediation work to remove historical mine sediments within the Leichhardt River. The Leichhardt River Remediation Project was completed in May 2008.

Given the findings and observations from this initial study future investigations should include:

- (i) Verification sampling to confirm the success of the subsequent Leichhardt River Remediation Project in removing the contamination;
- (ii) An investigation into the cause of ecological toxicity to aquatic species at the two sites adjacent to the velodrome;
- (iii) Confirmation of sites requiring further detailed ecological risk assessment.
- (iv) Completion of a more detailed study of bioavailability of heavy metals, particularly lead, using animal uptake studies to give a reliable and more refined human health risk assessment and verify the predictive potential of the bioaccessibility technique for bioavailability; and
- (v) Further development of knowledge on heavy metal pathways that may have the potential to impact on human health.

This study highlights the value of integrating human health and ecological health risk-based approaches to assess the significance of heavy metal and metalloid contamination.

Glossary

- Absolute Bioavailability (ABA) The fraction or percentage of a compound which is ingested, inhaled or applied to the skin that actually is absorbed and reaches systemic circulation
- **Absorption** The taking in or incorporation of something, such as a gas, a liquid, light, or heat
- Acute Exposure Exposure to a chemical for 14 days or less, may be either as a single or repeated dose
- **ADI** Acceptable Daily Intake. The daily intake of a chemical which, during a lifetime, appears to be without appreciable risk, on the basis of all the facts known at the time.
- **ANZECC** Australia and New Zealand Environmental Conservation Council
- **ANZECC guidelines** Guidelines for water and sediment quality, prepared by the Australian and New Zealand Environmental Conservation Council
- **ASTM** American Society for Testing and Materials
- Background Concentration Naturally-occurring, ambient concentrations in the local area of a site
- **Bioaccessibility (BAc** *in-vitro*) The soluble fraction under physiological conditions, i.e. an indicator of bioavailability to the receptor (e.g. humans)
- **Bioavailability (BA** *in-vivo*) The fraction of dose that reaches the systemic circulation of a receptor (e.g. humans). It is expressed as the ratio of the systemic dose to the applied dose, i.e. what is able to have an effect on the body compared to the total concentration to which it is exposed
- Chronic Exposure Repeated exposure to a chemical for a duration of three months or greater
- **Dermal** Of, or relating to, the skin or dermis
- **Dose-response relationship** The correlative association existing between the dose administered and the response (effect) obtained

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

- **EIL** Ecological Investigation Level
- **Exposure** Contact of a chemical, physical, or biological agent with the outer boundary of an organism (inhalation, ingestion or dermal contact)
- **Exposure Settings** Categories based on several conservative assumptions and are used to provide a 'tiered' set of soil criteria for different exposure settings:
 - 'A' = standard residential with garden/accessible soil
 - **'B'** = residential with substantial vegetable garden, and poultry
 - **'C'** = residential with substantial vegetable garden, excluding poultry
 - **'D'** = residential with minimal opportunities for soil access
 - **'E'** = parks, recreational open space and playing fields
 - **'F'** = commercial industrial
- **FAO** Food and Agricultural Organization of the United Nations
- g Gram
- **Guideline Values** Values, such as concentrations in soil, which are derived after appropriate allocation of Tolerable Intake (TI) among the possible different media of exposure
- **Hazard** The capacity of an agent to produce a particular type of adverse health or environmental effect
- HCI Hydrochloric acid
- **Health Risk Assessment** The process of estimating the potential impact of a chemical, biological, physical or social agent on a specific human population system under a specific set of conditions and timeframe
- HIL Health Investigation Level
- **ICP-MS** Inductively-coupled plasma mass spectrometry
- **ICP-OES** Inductively-coupled plasma optical emission spectrometry
- In-vitro Test tube test
- **In-vivo** Whole organism (animal) test
- **IPCS** International Programme on Chemical Safety of World Health Organisation (WHO)

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

- **ISQG-High** Australia and New Zealand Environmental Conservation Council Interim Sediment Quality Guidelines-High. Probable-effects concentrations below which biological effects in sediment would possibly occur. Concentrations at or above the ANZECC ISQG-High represent a probable-effects range within which effects in sediment would be expected to frequently occur.
- **ISQG-Low** Australia and New Zealand Environmental Conservation Council Interim Sediment Quality Guidelines-Low. Probable effects concentrations below which biological effects in sediment would rarely occur.
- **JECFA** Joint Food and Agricultural Organization of the United Nations / World Health Organisation Expert Committee on Food Additives
- M Molar concentration moles per litre
- mg/kg Milligrams per kilogram
- **mg/m³** Milligrams per cubic metre
- mL Millilitre
- NaHCO₃ Sodium bicarbonate
- NATA National Association of Testing Authorities
- **NEPC** National Environmental Protection Council
- **NEPM** National Environmental Protection Measure
- NHMRC National Health and Medical Research Council
- **OECD** Organisation for Economic Co-operation and Development
- **PBET** Physiologically based extraction test; an in vitro test for the measurement of bioaccessibility
- **pH** Negative logarithm of molar hydrogen ion concentration used as measure of acidity or alkalinity
- **Phytotoxicity** Toxic to plants

- **Pica** An abnormal craving or appetite for non-food substances, such as dirt, paint, or clay
- **Poisoning** The physiological state produced by absorption of excessive poison or other toxic substance
- **Rehabilitation** In the context of mining, 'rehabilitation' is described as returning the disturbed area to a stable and economically productive landform
- **Relative bioavailability** The comparative bioavailability of different forms of a chemical or for different exposure media containing the chemical and is expressed as a fractional relative absorption factor
- **Risk** The probability that, in a certain timeframe, an adverse outcome will occur in a person, group of people exposed to a hazardous agent
- **Sediment** The clay, silt or gravel carried by a flowing river or stream and deposited where the flow slows and results in alluvial deposition below the low water mark or up to the high water mark. Sediment comprises bed load material (>63 μm) that moves just above the bed and suspended material (<63 μm) that moves in suspension under the influence of turbulence. The fine sediment (<63 μm) is most representative for sampling purposes.
- **Soil** The part of the earth's surface consisting of humus and disintegrated rock that is located above the high water mark of an adjacent river or stream.
- Sub-chronic Exposure Repeated exposure to a chemical for a one to three month period
- **Titration** A common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant.
- **TWA** Time-weighted Average, average occupational exposure for an eight hour day/exposure period
- **TWI** Tolerable Weekly Intake
- **µg/m³** Micrograms per cubic metre
- **USEPA** United States Environmental Protection Agency
- WHO World Health Organisation

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

Table of Contents

Executive Summary	2
Executive Summary	3
Glossary	6
Table of Contents	10
1. INTRODUCTION	12
1.1 Purpose	. 12
1.2 Background	.13
1.2.1 The Lead Pathways Study	.13
1.2.2 Location	.13
1.2.3 Historical Contamination and Subsequent Remediation	. 13
1.2.4 Sampling Sites	. 14
1.2.5 Basis for Management of the Leichhardt River	. 17
2. METHODOLOGY	19
2.1 Collection of samples and analytical test methods	. 19
2.2 Sediment quality guidelines	. 20
2.3 Soil Investigation guidelines	.23
2.4 Assessment of ecological toxicity of sediment	.24
2.5 Assessment of human toxicity of soil	.27
2.6 Acid Generation Potential	.33
3. RESULTS	34
4. SITE SPECIFIC HEALTH RISK ASSESSMENT	42
4.1 Lead exposure pathways and subsequent risk calculations	.43
4.1.1 Dermal Exposure	.43
4.1.2 Dust Inhalation/Ingestion	.43
4.1.3 Oral Exposure	.45
4.1.3.1 Acute and Sub Chronic Exposure	.46
4.1.3.2 Chronic Exposure	.48
4.2 Arsenic Exposure Pathways and Subsequent Risk Calculations	.51
4.2.1 Dermal Exposure	.51
4.2.2 Dust Inhalation/Ingestion	. 52
4.2.3 Oral Exposure	.54
4.2.3.1 Acute and Sub Chronic Exposure	.54
4.2.3.2 Chronic Exposure	.56
5. DISCUSSION	60
5.1 Comparison of soil concentrations with NEPM HILs and EILs.	.60
5.2 Assessment against the sediment ISQGs	.64
5.3 Results for acid potential	.65
5.4 Significance of metals and metallolos to numan nealth	.05
0.4. I Leau	.00
0.4.2 AISENIC	.00
	.07
	00 70
1. PRUFESSIUNAL BAUKGRUUND	10

7.1 Centre for Mined Land Rehabilitation	70
7.2 Experience of consultants	70
8. LIMITATIONS	
9.0 REFERENCES	
10. APPENDICES	80
Appendix 1 Location of sampling sites	81
Appendix 2 Macroinvertebrate data summaries (Ecowise 2005, 2006)	
Appendix 3 Acid Potential Results	
Appendix 4 Acute Toxicity Assessment of Dry Sediment Samples to Two Cru	ustacean
Species and Aquatic toxicity heavy metals in elutriate results	92
Appendix 5 Summary Report on the completed Leichhardt River Remediation	ı Project
Works	118

1. INTRODUCTION

1.1 Purpose

The purpose of this study was to assess heavy metal and metalloid contamination within the Leichhardt River and the swimming pool / Kruttschnitt oval area at Mount Isa in order to understand the residual impact of historical pollution from mining activities and subsequent requirements for removal and rehabilitation.

When a site assessment indicates soil contaminants are present at concentrations above relevant guideline levels, a site-specific risk assessment may be conducted to address relevant human health and ecological concerns. The level to which such assessments are conducted depends on site-specific conditions (NEPC 1999).

In addition the National Water Quality Management Strategy and ANZECC (2000) water quality guidelines identify primary management aims for the protection of water resources and specify biological, water and sediment quality guidelines for protecting a range of aquatic ecosystems.

This is a focused study which aims to indicate the extent of the distribution of metal and metalloid contamination within the study area, and assess the potential resulting risk to human and ecological health. This is achieved through the following site assessment processes:

- The conduct of a limited sampling and analysis program to understand the distribution of contamination within an area previously known to be contaminated;
- The determination of the bioaccessible levels of heavy metals and arsenic using the PBET method (physiologically-based extraction test) and application of the bioaccessibility levels as a factor of total concentrations to give a bioaccessibility adjusted concentration;
- The completion of a desktop human health risk assessment using bioaccessibility as an indicator of bioavailability to understand the site-specific potential toxicity of lead and arsenic; and
- The comparison between sediment concentrations and ANZECC (2000) Interim Sediment Quality Guidelines (ISQG) as a measure of potential ecological toxicity.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

1.2 Background

1.2.1 The Lead Pathways Study

The Lead Pathways Study is a research program being conducted by The University of Queensland to investigate emissions to land, air and water at Mount Isa. In the wider study, the potential pathways of lead (primarily) and other heavy metals/metalloids into the community are being identified and any associated risks to human and ecological health determined. This study plays an important role in contributing information as to whether there are areas in the Mount Isa environment that are, or could become, sources of concern in regards to community and ecological health.

During the 1940s and 1950s, process tailings and other sediments originating from the Mount Isa Mines site, were deposited directly into the adjacent Leichhardt River system. At the time, river disposal, or at least no pro-active effort to prevent such disposal, was considered acceptable practice. Between 1991 and 1994, Mount Isa Mines Holdings in cooperation with the Mount Isa City Council and the Queensland Government CHEMUnit, undertook remedial works to remove mining sediments in areas adjacent to the town in the Leichhardt River. In a report by Mount Isa Mines Holdings entitled "Leichhardt River Stream Sediment Survey" (Mount Isa Mines 2003), the need for further remediation of the historical mine sediment deposition in the Leichhardt River between the Grace Street Bridge and the Alma Street crossing was identified. The Phase 1 (emissions to land) component, reported herein, was initiated in response to those recommendations.

1.2.2 Location

The Leichhardt River flows north into the Gulf of Carpentaria. At Mount Isa, the river (see Figure 1) is part of a fluvial system which is subjected to seasonal river flow and flooding during the annual wet season (November – March) and contraction of water to isolated pools during the dry season. The river fluvial material has a dry, exposed surface for most of the year.

Immediately downstream from Mount Isa is Lake Moondarra, the primary water supply for the town and local industry, including Mount Isa Mines. Lake Moondarra is also a popular recreational location for activities such as boating, fishing and swimming.

1.2.3 Historical Contamination and Subsequent Remediation

It is known that the sediments of the Leichhardt River have been contaminated by historical mining activities (Mount Isa Mines, 2003). Tailings discharges, use of waste rock for construction of infrastructure and reinforcing banks and storm water discharges have all contributed to the current sediment quality of the river.

Approximately 40,000 tonnes of tailings was discharged into the river during the 1940's and process wastes continued to be discharged into the river during the 1950's and 1960's (Mount Isa Mines, 2003).

Surveys conducted in 1973 to determine the extent of metal dispersion in sediments provided a useful background as to the state of the river prior to any significant remedial projects. There were then a number of sediment removal projects completed by the company throughout the 1970's, 80's and 90's leading to the removal of up to 100,000 tonnes of material from the river (Mount Isa Mines, 2003).

The Leichhardt River Management Plan was developed in 1993 as a joint project between the Mount Isa City Council (MICC), Queensland Government and Mount Isa Mines. The plan addressed a number of issues including historical contamination. Mount Isa Mines committed through this plan to remove any further contamination as it became exposed in the riverbed.

The 2002 survey (Mount Isa Mines 2003) showed that the sediment quality had improved markedly during the 29-year period since the last major 1973 survey, although there remained an area of concern between the Grace St Bridge and the Alma St crossing (Figure 1). The intensive surface sampling in this area in 2002 showed that a number of locations within this stretch of the river bed were in excess of the Queensland Environment Protection Agency investigation thresholds for Contaminated Land. It was recommended in 2002 (Mount Isa Mines, 2003) that some trenches be excavated in the river to determine the extent of contamination, and its subsequent removal once the extent of contaminated material was better defined.

1.2.4 Sampling Sites

The Phase 1 study has involved a focussed sampling exercise that provides a basis from which to develop an effective remediation strategy for the Leichhardt River and to provide an appropriate baseline from which the success criteria of future remediation campaigns could be assessed. The sampling sites were selected to show the range of heavy metals and metalloids, and their properties, over a large section of the Leichhardt River from upstream of the mine site to below Lake Moondarra. The river upstream of the mine was chosen as a background location, and samples thereafter from river locations at Death Adder Gully, between Grace St Bridge and Alma St crossing, downstream towards Lake Moondarra, and below Lake Moondarra.

In addition, limited sampling was undertaken at the swimming pool area to confirm the effectiveness of earlier remediation projects at this location. All sampling sites

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

for the Phase 1 study (Table 1 and Figure 1) corresponded to places of recreational activity and are non-residential locations.

It should be noted that the scope of this study was not to delineate the boundaries of any areas requiring remediation.

Site (LR = Leichhardt River)	Sample code	Sample category
LR - Upstream (background)	L1	Soil and Sediment
Death Adder Gully (West)	L2	Soil
Death Adder Gully (East)	L3	Soil
Skate Park (grassed area at depth) Swimming Pool Area	L4	Soil
Skate Park (ungrassed parking area) Swimming Pool Area	L5	Soil
Kruttschnitt Oval adjacent to Swimming Pool Area	L6	Soil
LR - Between Isa Street Crossing and Grace Street Bridge	L7	Sediment
LR - Historical Tailings (between Grace Street Bridge and Velodrome)	L8	Soil
LR - Downstream/East of Velodrome	L9	Sediment
LR - Velodrome East (Acid Generation Potential)	L10	Soil
LR - Velodrome West (Acid Generation Potential)	L11	Soil
LR - Pipe exit	L12	Sediment
LR - Historical Tailings West embankment	L13	Soil
LR - Historical Tailings deposition (mid channel)	L14	Soil
LR - Fluvial downstream (Moondarra)	L15	Sediment
LR - Downstream of Lake Moondarra (Leichhardt River)	L16	Sediment

 Table 1: Location of Sampling Sites



Figure 1: Soil / sediment sampling location points. Main map, red outlines indicate the targeted investigation area. Insert shows upstream and downstream sampling points, yellow rectangle shows extents of main map.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

1.2.5 Basis for Management of the Leichhardt River

It is important in understanding the context of the study that the key human and environmental values are identified. This study assesses the potential impact of metal and metalloid additions to the fluvial system on both human and environmental values in order that suitable and appropriate management practices be undertaken to ensure protection of both.

The broad objectives in terms of human values are to:

- Ensure the continued health and wellbeing of residents of the Mount Isa community; and
- Minimise the impact of mine sediments resulting from historical mining practices.

The purpose of undertaking a health risk assessment as part of this study is to identify and assess the significance of all potential exposure pathways for the entry of metals and metalloids into the human system. The assessment follows the potential pathways through to the endpoint (the human) to assess impact and risk. In addition, the relevance of historical mine sediment in the Leichhardt River, Mount Isa, as source of environmental exposure to the Mount Isa community needs to be considered.

The basis for undertaking a human health risk assessment of the soil component of the Leichhardt River is to compare the total concentrations of metals and metalloids against the National Environmental Protection Level (NEPM) Health Investigation Level (HIL) Level E (NEPC, 1999). This Investigation Level is considered to be the most relevant and applicable for this study as the sample sites corresponded to parks, recreational open space and playing fields. Residential sites were not a part of this Phase 1 study. The comparison of total metal and metalloid concentrations in soil assumes 100% bioavailability and may initially show that exceedances against the NEPM HIL Level E occurred at a number of sites. When the designated HIL is exceeded, the risk assessment process described by NEPC (1999) requires the undertaking of a Tier II risk assessment, including toxicity assessment.

On the ecological side, the pathway to the endpoint is more complex.

The objective adopted by ANZECC (2000) for the protection of aquatic ecosystems, and clearly of relevance to the Leichhardt River system, is to maintain and enhance the ecological integrity of freshwater (and marine) ecosystems, including biological diversity, relative abundance and ecological processes.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

ANZECC (2000) further identifies environmental values that are to be protected in a particular water body. The environmental values are site specific and are highly dependent on local factors including land use and the pre-existing condition of the catchment in terms of its relative position in the pristine-to-highly degraded continuum. In line with the ANZECC guidelines, the environmental values for the Leichhardt River at Mount Isa can broadly be defined as:

- Aquatic ecosystems;
- Stock water drinking;
- Recreation and aesthetics;
- Fishing;
- Water sports;
- Drinking water source; and
- Cultural and spiritual values.

For the environmental values of the aquatic ecosystem of the Leichhardt River, the key receptors requiring protection are the predators of macroinvertebrates, largely fish species. In turn, the fish are prey for the endpoint species of the food chain in the Leichhardt River ecosystem, the freshwater crocodile and scavenging birds such as eagles and kites.

This part of the study focuses on the aquatic sediment toxicity sampling to identify potential harm to macroinvertebrates, based on the assumption that a negative impact to the macroinvertebrate community will flow on to other species higher up the food chain hierarchy within the Leichhardt River ecosystem.

The study does not address the impacts of water quality on environmental values.

2. METHODOLOGY

The Leichhardt River fluvial material has a dry exposed surface for most of the year and is categorised as either sediment or soil based on the high water level mark during the wet season (ANZECC, 2000). For the purposes of assessment of impact from heavy metal and metalloid contaminants, collected samples of fluvial material can be processed as either sediment or soil depending on the objective of the particular assessment being undertaken. Samples from the swimming pool/ Kruttschnitt oval area at Mount Isa are categorised as soils.

In order to assess the potential impact to environmental and human values within the Leichhardt River system, this study has adopted the Australian water quality guidelines-sediment quality (ANZECC, 2000) for the assessment of sediments and the Investigation Levels for Soil (NEPC, 1999) for the assessment of soils. Collectively, these guidelines permit the evaluation and assessment of impact from heavy metal and metalloid contaminants in terms of human exposure and ecological effects.

2.1 Collection of samples and analytical test methods

Representative soil and sediment samples were collected on 30 March 2007 from upstream and downstream Leichhardt River and the swimming pool/ Kruttschnitt oval area at Mount Isa. In total, the collection of 13 soils, 6 sediments and 2 additional samples for analysis of acid generation properties, was undertaken (Figure 1, Table 1 and Appendix 1).

Soils were sampled according to NEPC (1999) and AS 4482.1 (Standards Australia 2005) to yield a <2 mm fraction from each whole collected soil sample. The <2 mm fraction of soil is the fraction defined to have the potential to be ingested via hand-to-mouth activities.

Sediments were sampled according to ANZECC (2000) to give a <63 μ m fraction from each whole collected sediment sample. In contrast to soil, sediment is collected as the <63 μ m fraction to give the most homogenous fraction of the whole sample that is relevant to ecological effects.

Physical properties of sediment such as grain size and density are important in sedimentation and transport processes. Typically, sediments are characterised as coarse material, clay/silt and sand fractions, on the basis of separations using 2 mm and 63 μ m sieves. Particles >2 mm may consist of shells, rocks, wood and other detrital materials, and are usually not a source of bioavailable contaminants. The clay/silt fraction has a high surface area and because of its surface chemistry

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

is more likely to adsorb organic and heavy metal contaminants. Particles <63 μ m are more common in the gut of sediment-ingesting biota. A significant metal fraction may be present in detrital, mineralized form (i.e. the >2 mm fraction), but this is generally considered of little ecological importance as it is usually unavailable for bioaccumulation (ANZECC, 2000).

Samples of about 1 kg were collected as a composite of 5 individual sub-samples, using a stainless steel scoop. The samples were contained in polyethylene zip lock bags and forwarded to Queensland Health Scientific Services Laboratory (NATA Accredited) in Coopers Plains, Brisbane following collection.

Soil and sediment samples were prepared according to the NEPC (1999), Standards Australia (2005) and ANZECC (2000) recommended procedures. Sediments and soils were dried at 60° C. The whole dried soils were sieved to separate the <2 mm size material which was then ground to <70 µm for analysis. The whole dried sediments were sieved and the <63 µm fraction was analysed.

The dried, sieved and ground samples were digested with aqua regia according to the USEPA (200.2) procedure, using aqua regia and total concentrations of metals/metalloids determined by ICP-OES (Queensland Health Scientific Services Laboratory). Sediment samples were also extracted with 1M HCI according to the ANZECC (2000) procedure for sediments, and analysed for metals/metalloids by ICP-OES to enable comparisons with the ANZECC (2000) ISQG-Low trigger values.

2.2 Sediment quality guidelines

A procedure for the development of appropriate sediment quality assessments is outlined in the ANZECC (2000) guidelines. Consideration of sediment quality follows a decision-tree approach (summarised in Figure 2) with a focus on identifying the issues and protection measures necessary to manage them. Interim Sediment Quality Guidelines (ISQGs) are trigger values that, if exceeded, prompt further action as defined by the decision tree. The two kinds of trigger levels that are indicated are: (i) ISQG-High which is defined as the probable-effects concentrations below which biological effects in sediment would possibly occur; and above which effects in sediment would be expected to frequently occur; and (ii) ISQG-Low which is defined as the probable-effects concentration below which biological effects concentration below which biological effects concentration below which is defined as the probable-effects concentration below which is defined as the probable offects in sediment would rarely occur.

As a first step, the total contaminant concentrations are compared with the ISQG-High and ISQG-Low trigger values (Table 2). If the low trigger value is exceeded and the concentration is greater than background levels, or the high trigger value is exceeded, then either management/remedial action or further investigation is required. Further investigation should consider the fraction of the contaminant that is bioavailable or can be transformed and mobilized into a bioavailable form

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

allowing comparison of contaminant concentrations adjusted for bioavailability with the ISQG-Low trigger value (Figure 2). In the case of metals and metalloids, the estimate of the bioavailable concentration by extraction with 1M hydrochloric acid (HCI) (ANZECC 2000) is likely to be a more meaningful measure than the total contaminant concentration. When the ISQG-Low trigger value is exceeded by the concentration once adjusted for predicted bioavailability, acute and chronic toxicity testing can be undertaken (Figure 2). Toxicity testing enables the response of the test organism to the bioavailable fraction to be assessed. The ISQG trigger levels are documented in Table 2.



Figure 2: Decision tree for the assessment of contaminated sediments (ANZECC, 2000)

2.3 Soil Investigation guidelines

The National Environment Protection (Assessment of Site Contamination) Measures (NEPMs) are the soil guidelines used in Australia to assess healthbased and ecological effects on a site-specific basis (NEPC 1999). A site may be assessed based on investigation levels, or a site specific assessment can be undertaken. The National Environmental Protection Council (NEPC) provides a framework for use of the investigation levels (NEPC, 1999) which are principally described as Investigation Levels and Response Levels.

Investigation Levels are generally either Health-based or Ecologically-based; Health Investigation Levels (HILs) and Ecological Investigation Levels (EILs). To accommodate the range of human and ecological exposure settings, a number of generic Investigation Levels have been set (NEPC, 1999). HILs and EILs are used for assessing existing contamination only and are intended to prompt an appropriate site-specific assessment where exceedances of investigation levels indicate there is the potential for adverse effects on human health or ecological values for that site. Before comparison with soil criteria, there should be sufficient characterisation of the site, and selection of appropriate Investigation Levels to ensure that the comparison is meaningful and appropriate.

In cases of minor exceedances of investigation levels or exceedances related to contaminants which have low human toxicity and limited mobility, a qualitative risk assessment may be sufficient. The risk assessment process (enHealth, 2004) may lead to the development of site-specific response levels generated by risk assessment and agreed in consultation between the professionals assessing the site and the regulatory authorities. The Tier II risk assessment process described by NEPC (1999) allows for toxicity assessment when HILs for the designated category or land use is exceeded. The NEPM Soil Investigation Levels are listed in Table 2.

The NEPM Soil Investigation Level that is considered to be relevant to this Phase 1 study is "Level E – Parks, recreational open space and playing fields including secondary schools". All sites sampled are used to varying degrees for recreation activities, and none of the sites are directly associated with residential activity.

The NEPM Ecological Investigation Levels (EILs) for Interim Urban are an indication of potential phytotoxicity only and do not apply to the Leichhardt River samples.

Table 2 ANZECC ISQG-Low and ISQG-High trigger values for sediments and NEPM Soil Investigation Levels (HIL = Health Investigation Level and EIL = Ecological Investigation levels)

Metal/ Metalloid	Soil HIL (Level A)	Soil HIL (Level D)	Soil HIL (Level E)	Soil HIL (Level F)	Soil EIL (Int Urban)	Sediment ISQG-Low	Sediment ISQG- High
Antimony (Sb)	NA	NA	NA	NA	_	2	25
Arsenic (As)	100	400	200	500	20	20	70
Cadmium (Cd)	20	80	40	100	3	1.5	10
Cobalt (Co)	100	400	200	500	_	NA	NA
Copper (Cu)	1,000	4,000	2,000	5,000	100	65	270
Lead (Pb)	300	1200	600	1,500	600	50	220
Manganese (Mn)	1,500	6,000	3,000	7,500	500	NA	NA
Nickel (Ni)	600	2,400	600	3,000	60	21	52
Zinc (Zn)	7,000	28,000	14,000	35,000	200	200	410

Level A - Standard residential with garden/accessible soil

Level D - Residential with minimal soil access

Level E - Parks, recreational open space and playing fields including secondary schools

Level F – Commercial/Industrial

2.4 Assessment of ecological toxicity of sediment

After examination of the soil and sediment results, an additional 3 kg of sediment was collected in August 2007 from the same sediment sample sites (Table 1). Samples were collected in clean polyethylene sampling zip lock bags, kept at 4^oC and forwarded to Ecotox Services Australasia (NATA Accredited), Lane Cove Sydney, NSW, for aquatic toxicity testing. As the sampling sites had remained dry and undisturbed in the intervening period (i.e. since e March 2007), the sediments were not reanalysed for metals and metalloids.

Selection of suitable test aquatic organisms for toxicity testing is governed by the available test species and fully-validated test methods that conform to USEPA, OECD and ASTM guidelines. For aquatic toxicity testing purposes, it is normally accepted that sensitive end-point species are identified that occupy key steps in the trophic chain (USEPA, 1998). ANZECC (2000) criteria also identify the need to protect species that have special significance in the aquatic ecosystem and recommend that a suite of organisms be used for aquatic testing purposes. The minimum that is recommended by ANZECC (2000) is an invertebrate, a fish and an alga. However, since fish are not applicable to aquatic toxicity testing of dried river sediment, they are not discussed any further in this context.

Prior to this study, an extensive aquatic ecosystem monitoring program to monitor freshwater fish and macroivertebrates was undertaken by Ecowise (2005, 2006) at six sites in a 60 km section of the Leichhardt River above and below the mine. The sampling was undertaken in March 2005 (Ecowise, 2005) and September 2005 (Ecowise 2006) corresponding to the late wet season and mid-late dry season, respectively.

Ecowise (2005, 2006) followed the Queensland Department of Natural Resources and Mines (NR and M 2001) AusRivAS (Australian River Assessment Scheme) protocols for rapid sampling of macroinvertebrates. The results were assessed against reference sites using the Qld AusRivAS model (NR and M, 2001). This protocol is based on the recommendation of ANZECC (2000) to use aquatic macroinvertebrates as the key biological indicator group for assessment of the health of Australian rivers and streams.

A total of 51 different macroinvertebrate taxa were collected during the 2005 program (Ecowise 2005, 2006). Of all the macroinvertebrates collected, Insecta were dominant (38 taxa), followed by Gastropoda (5 taxa) and Crustacea (4 taxa). The summary macroinvertebrate data is presented in Appendix 2.

As there were limitations to the use of the AusRivAS model with ephemeral streams, Ecowise was unable to provide an ecological assessment for the Leichhardt River sites. Advice from NR and M (the developers of the models) highlighted the limited reference data collected from the Mount Isa region to develop the models.

Univariate data analysis undertaken by Ecowise (2005, 2006) showed the sites to be in moderate to poor ecological condition, with average taxa richness. The seven taxa collected at all sites during both sampling events, were a mixture of moderately sensitive and pollution tolerant taxa. *Acarina* are considered to be moderately sensitive to poor water quality, while species such as *Corixidae* and *Pleidae* are air breathers and are not as susceptible to poor water quality.

During the September sampling event, the two control sites had dried out and taxa richness was higher at the impact (mine site) and recovery (downstream) sites. This result may be due to the surviving macroinvertebrates finding refuge in deeper waterholes during the dry season where the interaction of predation and competition can markedly alter community composition.

Despite the macroinvertebrate identifications undertaken by the studies of Ecowise (2006, 2006), the identification of suitable end or test species for aquatic toxicity testing of sediment, was not clear. The features that are needed for assessing the aquatic ecosystem of the Leichhardt River, and particularly the dry sediment habitat that exists for most of the year are: (i) a macroinvertebrate species that burrows and is compatible with high pH (8.0) and reasonable levels of salinity and

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

electrical conductivity (EC) arising from the presence of sulfate and chloride; and (ii) a species of macroinvertebrate that exists and emerges in water in contact with sediment and can be a food source to higher species e.g. fish.

In ephemeral waters, many aquatic macroinvertebrates have developed strategies to survive the dry periods when surface water disappears. Many organisms burrow down into the saturated sediments where interstitial water is permanently available. This aspect is considered to be of importance in selecting a suitable test aquatic organism for toxicity testing of the Leichhardt River sediments. There is also no validated aquatic toxicity test protocol for the macroinvertebrate species that exist in tropical northern Australia, including the Leichhardt River system.

The current lack of fully-validated test methods for tropical aquatic sediment macroinvertebrates that conform to USEPA, ASTM and OECD guidelines meant that an alternative approach to using local test species for sediment toxicity was required. To this end, Ecotox Services Australasia (Lane Cove, NSW) offered a NATA accredited service to undertake acute aquatic toxicity testing using two crustacean species, based on tests for sediments suggested by ANZECC (2000), as follows:

(i). 10-day whole sediment survival toxicity test using the estuarine amphipod *Corophium* spp., the only test species available for commercial ecotoxicity testing of sediment in Australia, and Test Protocol ESA SOP 109, based on USEPA (1996). *Corophium* spp. is a burrowing organism that is compatible with the high pH found in Leichhardt River water (pH 8.0), has been fully validated as a test species for both fresh and marine waters, is used internationally and is sensitive to heavy metals (Surtikanti and Hyne, 2000); and

(ii) 48-hour acute (survival) toxicity test using the freshwater cladoceran *Ceriodaphnia cf dubia* and Test Protocol ESA SOP 101, based on USEPA (1993). This species exists and emerges in water and can be a food source to higher species including fish. Tests were conducted on elutriate prepared from the dry sediment according to the US EPA procedure (US EPA, 1991), where sediment is mixed with dilution water at a ratio of 1:4, stirred and allowed to settle for two hours prior to preparation of a dilution series and seeding with test organisms.

Both species appear to be good model organisms for sediment toxicity assessment. However, lack of the minimum recommended number of species by ANZECC (2000) indicates that the response of the two test species can only be used to rank sediment samples in terms of potential toxicity.

Bulk samples of the sediments were forwarded to Ecotox Services Australasia and were used to undertake acute aquatic toxicity testing using the two crustacean species described above. The tests were commenced on 30 October 2007. The

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

metal concentrations in the elutriates from Ecotox Services were analysed by Advanced Analytical Australia Pty Ltd (NATA Accredited) in North Ryde, NSW.

2.5 Assessment of human toxicity of soil

When the HILs in soil are exceeded, it is recommended to undertake a risk assessment of the significance of the contamination.

In the absence of bioavailability data, it is usually assumed that metals (and metalloids, e.g. arsenic) are 100% bioavailable. In many cases, it has been demonstrated that bioavailability of contaminated soil is usually only a fraction of 100% (Ng *et al.*, 2003). It has been found that bioavailabilities (BA) of contaminants vary largely between site and the type of matrix (Freeman *et al.*, 1992; Ruby *et al.*, 1996). Therefore, the conduct of site-specific health risk assessments are the mechanism to provide the type and accuracy of information required.

Bioavailability is defined as the fraction of the administered dose that reaches the systemic circulation of an organism (NRC, 2003). This is determined using animal dosing (*in vivo*) experiments. In the *in vitro* system, bioavailability of a contaminant is referred to as bioaccessibility and is used as an alternative quantitative indicator of *in vivo* derived bioavailability estimates. Bioaccessibility as a measure of bioavailability has been evaluated by the USEPA (2007).

The measurement of bioavailability via animal uptake is expensive and time consuming. A more practical approach is to use the *in-vitro* PBET (physiologically based extraction test) (Ruby *et al.* 1996). PBET measures bioaccessible metal and metalloid concentrations and is an *in vitro* test that simulates extraction by the gastro-intestinal (GI) tract of a human being (Ruby *et al.* 1996) to predict the bioavailability (BA) of a substance or its absorption via the gut (Figure 3). PBET considers a range of stomach pH's to take into consideration varying bioavailabilities resulting from differing stomach conditions (e.g. fasting).

The PBET method has demonstrated good linear correlation with bioavailability in rats (lead and arsenic), rabbits (arsenic), cattle (arsenic), and monkeys (arsenic) (Ruby *et al.*, 1996; Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007). However, it has not been fully compared for the other metals. Bioaccessibility as measured by PBET gives a measure of all metals and metalloids that may be bioavailable from the ingestion of the tested mine waste and, in the absence of complete validation by comparison with animal uptake experiments, it is considered in this instance to be the best available estimate for health risk assessment purposes. While there are a number of other *in vitro* extraction tests available, such as the *in-vitro* gastric (IVG) (Rodriguez *et al.*, 1999), the simple bioaccessibility extraction test (SBET), the Method E Deutsches Institut fur Normung (DIN) model and the *in vitro* digestion

model, the simulator of human intestinal ecosystems of infants (SHIME) and the TIM (TNO-Netherlands Gastrointestinal Model) dynamic model (Oomen *et al.*, 2002), the PBET (Ruby *et al.*, 1996) was chosen for this study to determine the bioaccessibility (BAc) of heavy metals and arsenic as it is one of the few tests that has correlated well with a range of *in vivo* models. Bioaccessibility is defined as the soluble fraction under physiological conditions, i.e. an indicator of bioavailability to the receptor (e.g. humans).

	Stomach Phase			Intestinal Phase
	Fasted- solution	Average- solution	Fed- solution	Small Intestine
	_1	2	3	
pH:	1.3	2.5	4.0	7.0

Figure 3: Conceptual representation of the gastro-intestinal phases which are tested by PBET

Although PBET has been adopted as an alternative means of predicting bioavailability, it is recognised that BAc, is more conservative compared to the measurement of bioavailability (BA *in-vivo*) using rat as an uptake model. The studies of Bruce *et al.* (2007) and Diacomanolis *et al.* (2007) have shown that BAc can be up to 10 times higher than the actual bioavailability (BA *in-vivo*) for lead, and 5 times higher for arsenic (see Tables 3 and 4 and Diacomanolis *et al.*, 2007). For validation purpose, BA *in-vivo* was determined using a rodent feeding model for composite sample category.

 Table 3:
 Bioaccessibility % (BAc %) of four different categories of mine waste

 materials determined by PBET

Mine waste material	Arsenic (BAc % of total metalloid)	Lead (BAc % of total metal)
Category 1	8.1 ± 1.6	10.2 ± 1.5
Category 2	8.5 ± 4.3	13.2 ± 2.1
Category 3	3.9±1.1	13.4±2.6
Category 4	3.9±0.5	11.9±1.3

Table 4: Comparison of bioaccessibility (BAc %) with actual bioavailability (BA *in-vivo* %) showing conservative nature of BAc

Elements	BA	BAc % of total
	in-vivo %	metal/metalloid
Arsenic (As)	1.6-1.9	3-10
Lead (Pb)	0.6-1.4	10-18

For the purpose of this study, the more conservative estimates (BAc) of potential intake of heavy metals and arsenic were used as the levels against which the site-specific human risk assessments were undertaken. Although *in vivo* models more closely reflect physiological conditions, the simple cost-effective *in vitro* extraction test based on human physiological conditions, PBET, was adapted for this study.

The PBET was undertaken on samples ground to <70 µm and oven dried for approximately 10 h at 50°C in a vacuum oven prior to being weighed. The *in vitro* reactor design employed for PBET was similar to that described by Ruby et al. (1996). In order to simulate stomach mixing, an inert gas (argon) was purged through the reaction mixture at approximately 0.7 L/min. This flow rate was less than the 1.07L/min described by Ruby et al. (1996), although the reaction vessels used in this experiment were smaller. Thirty mm (diameter) glass round-bottom tubes, 120 mm in length and fitted with rubber bungs, were used as reaction vessels. Each rubber bung was fitted with a stainless steel tube approximately 2 mm internal diameter to deliver the argon gas, and a one-way pressure valve (bicycle tyre valve) (Figure 4). Detachable polyethylene gas lines were connected to the stainless steel gas delivery tube, after passing through a water trap to heat the gas prior to mixing the reactants. Gas flow was calibrated periodically using a gas flow meter. Each sample for PBET was replicated four times, and all reaction vessels were partially submerged to above the reaction mixture volume in a temperature-controlled water bath maintained at 37°C. The 120 mL glass reaction vessels were used to simulate the GI environment during the PBET determination. The samples were allowed to equilibrate at 37°C for 10 min prior to the introduction of argon gas which was used to provide the physical mixing within the reaction vessel.



Figure 4: The 120 mL glass reaction vessels used to simulate the GI environment during the PBET. (A) the sample is allowed to sit for 10 min prior to the introduction of argon gas; (B) the bubbled argon is used to create a mixing environment

Gastric solution for PBET was prepared using the same recipe as that outlined in Ruby *et al.*(1996): 1.25 g of pepsin (Sigma Chemical Co.), 0.5 g of sodium citrate (MERCK, Germany), 0.5 g of malic acid (Sigma Chemical, USA), 420 μ L of lactic acid (Sigma Chemical Co.), and 500 μ L of acetic acid (BDH, Australia) was added to 1 L of deionised water (Milli-Q) and mixed gently for approximately 1 min. Three separate batches of the gastric solution were prepared and each was adjusted to the selected pH using concentrated (10N) HCl. The pH values selected reflect those used by Ruby *et al.* (1996), and are based on the "fasting (empty stomach), pH 1.3", "average (with some food ingestion), pH 2.5" and "fed (full stomach), pH

4.0" pH states of a human stomach, and pH 7 reflects the small intestinal pH in humans (Figure 3). All pH states (1.3, 2.5, 4.0 and 7.0) were tested during PBET analysis of the waste material, in order to simulate various physiological states of the gastro-intestinal tract of a normal human being. An average BAc from all pH conditions is taken as a representative BAc of the tested material.

Variation in the measure of bioaccessibility by PBET of arsenic, chromium, nickel, cadmium, and lead, as a function of liquid-to-solid ratio, was evaluated by Hamel *et al.* (1998). These authors determined the BAc in synthetic gastric juices was affected only slightly by changes in the liquid-to-solid ratio in the range of 100:1 to 5000:1 (mL/g).

A liquid-to-solid ratio of 100:1 (mL/g) was used for PBET. The gastric solution (30 mL) was added to a reaction vessel and combined with 0.1 g of solid material. Four replicates of each of the three different stomach and one small intestine solutions were used for each material (n = 12). The pH of the $37^{\circ}C$ mixture being purged with argon gas was then checked after 5 min and adjusted with HCl or saturated NaHCO₃ if necessary to maintain the selected pH environment. The pH was then checked again after 10 min and every 20 min thereafter. One mL samples of the mixture were collected at 20, 40 and 60 min after the argon was introduced. Each time the mixture was sampled, an equal volume was replaced from the stock solution of the appropriate gastric solution, to maintain the initial 30 mL volume. After 1 hr, all mixtures were titrated to pH 7.0 using a saturated NaHCO₃ solution, rather than a suspended dialysis bag as used by Ruby et al. (1996). At this stage, 70 mg of porcine bile salts (Sigma Chemical Co.) and 20 mg of porcine pancreatin (ICN Biomedicals, Australia) were added to the mixture to reflect the small intestine conditions. Samples were taken from all reaction vessels 3 hr after titration to pH 7.0. All samples were centrifuged immediately after collection at 10,000 rpm (10,000 x gravity) for 15 min in a IEC MicroMax Centrifuge (IEC, Massachusetts, ASA), and the liquid fraction was then filtered through a disposable 0.22 µm Millipore filter to remove any remaining mine waste material. Elemental analysis of the filtrate was undertaken by ICP-MS.

The bioaccessibility % (BAc %) is calculated using the following equation.

$BAc\% = \frac{\text{concentration of the element solubalised from the media}}{\text{concentration in the media before extraction}}$

For quality control purposes, blanks including only the gastric solution were sampled using the above protocol. In addition, an in-house tailing sample from Mount Isa (Pb = 34,080 mg/kg) was included in triplicate for each batch run (Table 5).

Table 5: Quality control for PBET for the measurement of bioaccessibility % (BAc %) in triplicate for copper, zinc, cadmium, arsenic and lead using a homogenised in-house (IH) tailing sample with a lead concentration of 34,080 mg/kg. The results show mean BAc %, standard deviation (SD), intra-assays (cv) and inter-assays (CV) coefficient of variation.

Intra-assays	Cu	Zn	Cd	As	Pb
Day 1 BAc%	19.0	25.0	53.7	1.2	9.8
SD	4.2	5.7	5.0	0.3	2.2
%cv	21.9	22.8	9.3	28.1	22.7
Day 2 BAc%	19.7	25.9	52.0	1.3	10.1
SD	4.7	6.5	1.2	0.3	2.8
%cv	23.9	25.1	2.3	19.8	27.4
Day 3 BAc%	22.0	26.8	43.2	1.2	7.9
SD	3.2	2.4	3.9	0.2	0.4
%cv	14.8	8.8	9.1	18.7	5.3
Day 4 BAc%	17.6	22.8	46.0	1.0	8.8
SD	1.5	2.4	4.7	0.1	0.8
%cv	8.3	10.5	10.2	10.2	9.6
Day 5 BAc%	16.8	22.2	48.1	1.1	9.8
SD	2.5	4.5	3.2	0.1	1.6
%cv	14.9	20.5	6.7	10.5	16.3
Day 6 BAc%	17.6	20.7	52.4	1.2	9.2
SD	0.9	3.1	7.3	0.1	1.3
%cv	5.1	15.2	13.9	10.3	14
Inter-assays	18.8	23.9	49.2	1.2	9.3
SD	1.9	2.4	4.1	0.1	1.7
%CV	10.0	9.9	8.4	8.5	18

The variation in the data in Table 5 is considered to be acceptable considering the number of steps, the pH values employed for the PBET and the subsequent ICP-MS analysis.

2.6 Acid Generation Potential

Samples were collected from two locations (Sites L10 and L11) where waste rock was historically placed in the river, and appeared to be visibly oxidising. Composite 1 kg soil/sediments and were sent to Australian Laboratory Services Pty Ltd (ALS) Stafford, Queensland, for measurements of acid generation properties using standard methods listed below:

- Net acid production potential (NAPP) (ALS Method EA009);
- Net acid generation (NAG) (ALS Method EA011);
- Acid neutralising capacity (ANC) (ALS Method EA013);
- pH (saturated paste) (ALS Method EA031);
- Electrical conductivity (saturated paste) (ALS Method EA032); and
- Total sulfur by LECO (ALS Method EA042T).

3. RESULTS

The results for total digested concentrations and bioaccessibility for soil and sediment samples are given in Table 6.

	Cobalt Total Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg	Nickel Total Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg	Copper Total Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg
L1 Soil	7.6	9	0.68	7.2	<1	0.072	13.9	38	5.3
L2 Soil	49.3	24	11.8	16	11	1.76	4096	48	1970
L3 Soil	52	22	11.4	23.8	11	2.62	4380	46	2020
L4 Soil	11	22	2.4	10.7	5	0.54	214	25	53.6
L5 Soil	13.4	20	2.9	13.7	4	0.55	511	39	199
L6 Soil	14.9	30	4.5	16.4	6	0.98	554	46	255
L8 Soil	44.2	23	10.2	10.6	64	6.78	1344	23	309
L10 Soil	12.8	40	5.1	8.3	63	5.23	382	21	80.3
L11 Soil	247	49	121	19.7	99	19.5	10900	25	2718
L13 Soil	49.8	19	9.5	9.6	68	6.5	1035	17	176
L14 Soil	6.1	32	2.0	5.2	6	0.31	61.2	67	41.0
L15 Soil	16	12	1.9	17	7	1.2	201	33	66.3
L16 Soil	28.9	5	1.5	27.8	4	1.1	69.7	3	2.1
L1 Sediment	21.5	11	2.4	29.6	6	1.8	96.9	5	4.8
L7 Sediment	21.3	11	2.3	56.9	6	3.4	554	19	105
L9 Sediment	24.1	9	2.2	28.6	14	4.0	447	16	71.5
L12 Sediment	86.1	13	11.2	37.3	51	19.0	17300	19	3290
L15 Sediment	26	8	2.1	26	6	1.6	321	13	41.7
L16 Sediment	32.7	6	2.0	36	5	1.8	120	3	3.6

Table 6: Results for total concentration and % bioaccessibility (BAc %) of soils and sediments

Note : <DL is below detection limit; when applying the bioaccessibility factor to the total concentration, where the bioaccessibility is <n then the maximum possible figure is used (for example where the BAc is <1 it is taken to be 1)

Table 6 continued

	Zinc Total Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg	Arsenic Total As Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg	Cadmium Total Conc. mg/kg	BAc %	Resultant BAc Conc. mg/kg
L1 Soil	17.1	81	13.9	2	10	0.2	0.1	<1	
L2 Soil	1890	37	698	198	9	17.8	8.8	39	3.43
L3 Soil	1370	32	439	207	10	20.7	8	39	3.12
L4 Soil	104	16	16.6	8	17	1.36	0.2	10	0.02
L5 Soil	303	28	84.8	20	15	3	3.8	42	1.60
L6 Soil	277	45	125	11	24	2.64	2.8	45	1.26
L8 Soil	49400	35	17280	480	1	4.80	137	38	52.2
L10 Soil	2460	54	1330	247	<1	2.47	4.1	46	1.89
L11 Soil	7780	44	3420	397	4	15.9	20.9	34	7.12
L13 Soil	30240	35	10600	541	1	5.41	186	35	65.0
L14 Soil	432	32	138	6.8	12	0.82	5.5	41	2.26
L15 Soil	350	9	31.5	5.9	16	0.94	3.1	24	0.74
L16 Soil	107	<1	1.66	3	1	0.03	0.3	<1	0.003
L1 Sediment	94.2	<1	0.94	9	4	0.36	0.1	8	0.008
L7 Sediment	252	5	12.6	115	2	2.29	1.9	23	0.44
L9 Sediment	476	19	90.4	21.9	4	0.88	3.1	23	0.71
L12 Sediment	6700	33	2210	341	11	37.5	132	38	50.2
L15 Sediment	467	6	28.0	21.6	5	1.08	3.2	22	0.70
L16 Sediment	147	<1	1.47	3	4	0.12	0.2	3	0.006

	Antimony Total Conc.	BAc	Resultant BAc Conc.	Lead Total Conc.	BAc	Resultant BAc Conc.
	mg/kg	%	mg/kg	mg/kg	%	mg/kg
L1 Soil	<dl< th=""><th><1</th><th>-</th><th>5</th><th><1</th><th>0.05</th></dl<>	<1	-	5	<1	0.05
L2 Soil	6.9	10	0.69	2172	14	304
L3 Soil	0	<1	0	2463	12	296
L4 Soil	<dl< th=""><th><1</th><th>-</th><th>66.7</th><th>1</th><th>0.67</th></dl<>	<1	-	66.7	1	0.67
L5 Soil	<dl< td=""><td><1</td><td>-</td><td>340</td><td>8</td><td>27.2</td></dl<>	<1	-	340	8	27.2
L6 Soil	<dl< th=""><th><1</th><th>-</th><th>290</th><th>11</th><th>31.9</th></dl<>	<1	-	290	11	31.9
L8 Soil	1080	1	1.07	25010	16	4000
L10 Soil	9.9	4	0.40	6600	17	1120
L11 Soil	10.8	29	3.13	6710	16	1070
L13 Soil	137	1	1.37	41900	24	10050
L14 Soil	<dl< td=""><td><1</td><td>-</td><td>293</td><td>20</td><td>58.5</td></dl<>	<1	-	293	20	58.5
L15 Soil	<dl< td=""><td><1</td><td>-</td><td>187</td><td>5</td><td>9.4</td></dl<>	<1	-	187	5	9.4
L16 Soil	<dl< th=""><th><1</th><th>-</th><th>31.5</th><th><1</th><th>0.32</th></dl<>	<1	-	31.5	<1	0.32
L1 Sediment	1	<1	0.01	46	<1	0.46
L7 Sediment	1	15	0.15	3023	6	18.1
L9 Sediment	2	1	0.02	232	5	11.6
L12 Sediment	10.9	71	7.74	20000	25	5000
L15 Sediment	2	3	0.06	467	5	23.3
L16 Sediment	1	<1	0.01	49.9	<1	0.50

Table 6 continued

It can be seen from Table 6 that there is a wide range of total concentrations for all heavy metals and metalloids; copper 13.9-19,300 mg/kg, zinc 17.1 - 49,400 mg/kg, arsenic 2-541 mg/kg, cadmium 0.1- 186 mg/kg and Lead 5 - 41,900 mg/kg. The bioaccessibilities also vary significantly. For lead the maximum bioaccessibility is 25%.

Figure 5 shows a comparison of total (left) and bioaccessibility adjusted (right) soil lead concentrations. The red circles denote samples exceeding NEPM HIL- Level E and indicate that four sites remain in exceedance when the bioaccessibility adjusted soil lead concentration is compared against the Level E criteria. Figure 6 shows a similar comparison for arsenic but shows that no sites remain in exceedance of the NEPM HIL Level E criteria when soil arsenic concentration is adjusted for bioaccessibility.

The data displayed in Figures 5 and 6 reflect the application of the more accurate health risk assessment approach using bioaccessibility adjusted soil concentrations.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009


Figure 5: Total (left) and bioaccessibility adjusted (right) soil lead concentrations. Insert shows results for soil samples taken upstream and downstream of the town. Yellow box in insert shows location and size of main map. Red circles denote samples exceeding NEPM HIL-E level.



Figure 6: Total (left) and bioaccessibility adjusted (right) soil arsenic concentrations. Insert shows results for soil samples taken upstream and downstream of the town. Yellow box in insert shows location and size of main map. Red circles denote samples exceeding NEPM HIL-E level.

Sediment total concentration data (Table 6) are compared against the ISQG-High and ISQG-Low trigger values (Table 2). Sediments are also extracted with 1M of hydrochloric acid (HCI) so that an estimate of bioavailable concentrations can be compared against the ISQG-Low trigger values. The results for 1M HCI extraction of sediment are given in Table 7.

	Cobalt 1 M HCI mg/kg	Nickel 1 M HCI mg/kg	Copper 1 M HCI mg/kg	Zinc 1 M HCI mg/kg	Arsenic 1 M HCI mg/kg	Cadmium 1 M HCI mg/kg	Antimony 1 M HCI mg/kg	Lead 1 M HCI mg/kg
L1 Sediment	5.2	3	30	22.6	<0.1	<0.1	<0.1	32.2
L7 Sediment	7.2	22.2	266	118	10	1.5	<0.1	257
L9 Sediment	10.3	4	228	309	1.1	2.7	<0.1	188
L12 Sediment	36.1	15.7	6400	4290	174	111	<0.1	20000
L15 Sediment	6.8	2.6	128	271	<0.1	2.6	<0.1	406
L16 Sediment	6.5	2.5	26.3	47	<0.1	0.1	<0.1	41.9

Table 7: Sediment extraction with 1M Hydrochloric Acid

Note : <DL is below detection limit

Site L12 is found in the sediment extraction to have the highest levels of metals (copper 6,400 mg/kg, zinc 4,290 mg/kg, arsenic 174 mg/kg, cadmium 111 mg/kg and lead 20,000 mg/kg). Elevated levels were also recorded at Sites L7, L9 and L15, although substantially lower than found at L12.

The results for acid potential measurements are presented in Table 8 and Appendix 3. Samples along the eastern and western sides of the Velodrome in the Leichhardt River (Sites L10 and L11) showed that there was high acid-producing potential at L10 but the material only oxidised slowly as the saturated paste test did not show acid pH. At Site L11 there was no acid-producing potential and no generation of acid indicated from the saturated paste test.

Test	Limit of Reporting	Units	L10 Soil	L11Soil
Nett Acid Producing Potential	0.5	kg H₂SO₄/t	122	-15
pH (OX)	0.1	pH unit	7.8	7.9
NAG (pH 4.5)	0.1	kg H₂SO₄/t	<0.1	<0.1
NAG (pH 7.0)	0.1	kg H₂SO₄/t	<0.1	<0.1
Acid Neutralising Capacity ANC as H ₂ SO ₄	0.5	kg H₂SO₄ equiv.	57.9	99.2
Fizz rate	1	Fizz Unit	2	2
pH (saturated paste)	0.1	pH Unit	5.9	6.9
Electrical Conductivity (saturated paste)	1	μS/cm	3450	3510
Total Sulfur by LECO Sulfur – Total as S	0.01	%	5.89	2.75

Table 8:	Results for Acid	l Potential	measurements

Tables 9 and 10 give the aquatic toxicity test results for both the 48-hr Acute (Survival) toxicity test using the freshwater cladoceran (*Ceriodaphnia cf dubia*) in sediment water elutriate (sediment mixed with dilution water 1:4; filtered <0.45 μ m) and the 10-day Whole Sediment survival toxicity test using the estuarine amphipod (*Corophium spp*). Appendix 4 gives the complete results for toxicity testing.

Table 9: Aquatic toxicity test results; 48-hr Acute (Survival) toxicity test using the freshwater cladoceran (*Ceriodaphnia cf dubia*) in sediment water elutriate (sediment mixed with dilution water 1:4; filtered <0.45 μ m).

Concentration (%)	% Survival at 48 hr					
	L1	L7	L9	L12	L15	L16
0 (control)	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0
6.25	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0	100±0.0
12.5	100±0.0	100±0.0	0±0.0	0±0.0	100±0.0	100±0.0
25	100±0.0	100±0.0	0±0.0	0±0.0	100±0.0	100±0.0
50	100±0.0	100±0.0	0±0.0	0±0.0	100±0.0	100±0.0
100	100±0.0	100±0.0	0±0.0	0±0.0	100±0.0	100±0.0

Table 10: Aquatic toxicity test results; 10-day Whole Sediment survival toxicity test using the estuarine amphipod (*Corophium* spp.)

	Control	L1	L7	L9	L12	L15	L16
% Survival at 10 days	92.5±5.0	75.0±12.9	90.0±8.2	0.0±0.0	0.0±0.0	82.5±15.0	90.0±0.0

The results of the two toxicity tests showed similar results. In each test all Sites excluding L9 and L12 showed little or no indication of toxicity. However, L9 and

L12 each had 100% death rates in all scenarios except for the 48-hr acute toxicity test at 0% and 6.25% concentrations. The toxicity tests do not specifically identify the toxicant causing ecotoxicity.

Table 11 presents the heavy metal and arsenic concentrations in sediment water elutriate (sediment mixed with dilution water 1:4; filtered <0.45 μ m) used in Table 9.

Table 11: Metal and metalloid concentrations in sediment water elutriate (sediment mixed with dilution water 1:4; filtered <0.45 μ m)

Sample Number	Arsenic mg/L	Cadmium mg/L	Copper mg/L	Lead mg/L	Zinc mg/L
L1	<0.02	<0.001	0.002	<0.006	<0.003
L7	<0.02	<0.001	0.007	<0.006	0.012
L9	<0.02	0.11	0.12	0.39	0.78
L12	<0.02	0.22	1.6	2.1	< 0.003
L15	<0.02	<0.001	0.003	<0.006	0.003
L16	<0.02	<0.001	0.002	<0.006	<0.003
Control	< 0.02	<0.001	< 0.001	<0.006	< 0.003

Note : <DL is below detection limit

Two of the samples, L9 and L12, had significantly greater solubility of metals when the sediment was mixed with water to give an elutriate, than any of the other sediments. Whilst the heavy metal and arsenic concentrations are significantly greater at L12 than any other sites, L9 has similar and in some cases lower total concentrations of metals than the other sediments.

4. SITE SPECIFIC HEALTH RISK ASSESSMENT

The purpose of this health risk assessment is to identify and assess the significance of all potential exposure pathways for the entry of lead and arsenic into the human system. In addition it looks at the relevance of historical mine sediment in the Leichhardt River, Mount Isa, as source of environmental exposure to the Mount Isa community.

The following risk assessment is largely based on a residential scenario, hence is an exceptionally conservative measure of the risk from the samples taken in the river and even those from the swimming pool and skate park area. The area of the Leichhardt River which was sampled is not a high traffic area. However, three mechanisms by which people may be exposed to this material are through:

- Recreational activities within the river;
- Fine dust from soils and sediments within the river being blown into residential areas, where it contributes to dust in air and is deposited on the ground; and
- Historical use of sediments removed from the river on residential properties.

Notwithstanding the conservative scenario, however, a generic health risk assessment for arsenic and lead exposure as conducted here provides a set of 'look up tables' for contamination levels in the soil/dust above which ADI (acceptable daily intake) should not be exceeded.

The exposure routes considered here include dermal/skin, inhalation and oral exposure. For a holistic risk assessment, intake of contaminants from the normal daily diet and drinking water are also included. Because of the close proximity of the mine to the residential areas of Mount Isa, it is extremely important that the contribution from the mining operations to exposure in the community is well understood.

The main sources of exposure are more likely to be from dust and soils with elevated levels of lead and arsenic. Situations have been identified elsewhere in Australia and around the world in similar industry settings such as Port Pirie, South Australia, where mining and processing operations can be significant sources of environmental exposure to the receptors, including humans, via emissions and dust fall-out.

Although PBET (bioaccessibility measurement i.e. BAc) has been adopted as an alternative means to predict bioavailability, it is recognised that BAc measured using PBET is a more conservative estimate compared to absolute bioavailability

(ABA) measured using rat animal uptake as discussed in Section 2.5. In summary, the Phase I study uses the more conservative estimate (BAc) of potential intake of arsenic and lead. A more accurate site specific determination of exposure (particular for Pb) can be obtained by measurement of bioavailability data as illustrated in Tables 3 and 4 (Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007). This can be considered in future studies.

The wider study (Phase 2 in progress) on types of waste materials from the mining operations, natural mineralisation and residential soil/dust will help to clarify the most likely main source and extent of contributions to overall blood lead loading in young children. This will help to formulate an effective management strategy for the minimisation of lead exposure to the population in Mount Isa.

4.1 Lead exposure pathways and subsequent risk calculations

4.1.1 Dermal Exposure

Although the risk associated with dermal exposure to metal/metalloid bearing soils are not well quantified (Holmes *et al.*, 1999), the dermal absorption of inorganic lead through undamaged human skin is considered to be minimal compared to alternative routes of entry (IPCS, 1995; ATSDR, 2000).

The correlation of lead in blood from factory workers compared to their associated dermal exposure has been conducted to investigate dermal absorption. Results confirm that there was no indication that lead was subsequently absorbed through the dermal layers (Sun *et al.*, 2002). When considering exposure to lead from solid matrices such as soil, there is no mechanism for absorption of such elements attached to soil particles through intact skin (NRC, 2003). When the dermal barrier is compromised through disease or physical injury, the permeability of the skin is increased (NRC, 2003).

For the purpose of this investigation it can be concluded that the dermal exposure to lead is probably insignificant.

4.1.2 Dust Inhalation/Ingestion

The inhalation of dust containing lead is an important consideration in industrial settings such as smelters, and chemical plants, and lead-acid battery manufacturing (ATSDR, 1999). Here, there may be airborne particles of lead bound to fine particles (<1 μ m) in the occupational environment (IPCS, 1995). Larger particles (1 - 5 μ m) will usually lodge at different regions along the respiratory pathway during inhalation, and are eventually moved up into the oral

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

cavity and swallowed. Smaller particles (<1µm) will often lodge as far as the alveoli, and may also be moved out of the lungs and swallowed or alternatively absorbed directly into the lymphatic system.

The following calculation is used to determine if elevated levels of lead in soil contribute a significant source of lead in the home by inhalation. The calculation (Ng, 1999) assumes a worst case scenario; that the whole of the airborne dust contains only the soil particles with the highest Pb concentration identified in the sampling program (Table 6) at 41,900 mg/kg (μ g/g) and that people are breathing in this dust eight hours a day and five days a week.

The following guidelines are used as a basis of the calculation:

1. The recommended allowable house dust level (indoor air total suspended particulates) in the indoor air is **90 \mug/m³** (**90 x 10⁻⁶ g/m³**), according to the Interim National Indoor Air Quality Goal Recommended by NHMRC (NHMRC, 1990).

2. Time-weighted average (TWA) concentration of lead (as inorganic dust and fumes, as Pb) over an eight-hour working day, for a five-day working week has been set at **0.15 mg/m³ (150 \mug/m³)** for the occupational environment by Worksafe Australia (1995).

These two assumptions are applicable to residential occupancy where adults and children may be located on a continuous basis.

The calculation is based on the assumption that the dust level is at the highest amount of 90 μ g/m³ (90 x 10⁻⁶ g/m³), as indicated above.

If the highest lead concentration in the soil/dust was **41,900** mg/kg (μ g/g) (L13) the lead level in the air (Pb_{air}) at the site of specified soil concentration is calculated using Equation [1] below:

Equation [1]:

 Pb_{air} = Soil concentration (mg/kg) x Recommended allowable dust level (90x10⁻⁶ g/m³ NH&MRC 1990) = Concentration in air (µg/m³)

 $Pb_{air} = 41,900 \text{ mg/kg} (\mu g/g) \times 90 \times 10^{-6} \text{ g/m}^3 = 3.77 \ \mu g/m^3$

The TWA safety factor (SF) can then be applied to determine the likelihood of influence.

SF = (**150 µg/m³**)/3.77 µg/m3 = **39.8**.

Based on the above assumptions, the dust in air directly derived from the source of the highest concentration of lead (41,900 mg/kg) sampled, would be **39.8** times below the recommended TWA value for occupational exposure of lead.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

The above risk assessment for the dust is conservative, since one assumes the worst case scenario; these calculations are based on 100% pulmonary bioavailability, and assume that concentration of lead in dust is the same as concentration of lead in a single source. Hence, it is anticipated that both the exposure and the uptake could be expected to be significantly reduced.

One would expect the dust level at the residential area is lower than that of the occupational setting. However, if the assumption is made that the high dust level is the same in the residential area and that some residents (e.g. home-bound people, young infants and recent mothers) are exposed to the same lead level 24 hours of a day the safety factor will be 3 fold less than that calculated above. This still amounts to a safety factor of about 13 assuming the highest air-borne soil lead (Pb_{air}) is 41,900 mg/kg at the specific site. The exposure and the risk are reduced even further in areas that are recreational rather than residential.

It is concluded that even where there are exceptionally high levels of lead in soil the dust is not considered to be hazardous to the humans via inhalation alone. Having said this, during periods of dust creation, such as earth moving, personal precautionary measures can be used, as in any dusty environment, to reduce exposure even further.

4.1.3 Oral Exposure

Oral exposure refers to the movement of materials to the mouth resulting in ingestion. Sources include food and drink as well as any material that might be inadvertently put in the mouth. For example, someone eating without washing their hands has increased likelihood of transferring contaminants to the food and ingesting it. The likelihood of uptake of contaminants is increased in children who put objects into their mouth, suck on things, and/or eat dirt material (this refers to hand-to-mouth activities in the literature).

The following component of the risk assessment calculates the amount of lead absorbed by the body based on an expected rate of ingestion, a range of concentrations of lead in soil, and a range of bioavailabilities which is then compared against relevant impact levels for acute, sub-chronic and chronic exposure to determine the risk.

It should be noted that soluble lead compounds are generally more bioavailable than the insoluble ones for absorption via the oral route. For mineral - based waste materials the absolute bioavailability (ABA) of lead-contaminated soil is likely to be less than 10% (Bruce *et al.*, 2007; Diacomanolis *et al.* 2007). For a conservative estimate, an ABA of up to 25% is employed here for illustration purposes. The 25% level chosen for ABA is also the highest level of BAc found in the samples tested. As mentioned above, BAc is more conservative than ABA.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

4.1.3.1 Acute and Sub Chronic Exposure

Acute exposure refers to an exposure period of 14 days or less (ATSDR, 1999). In order to quantify the human health risk from acute lead exposure, acute toxicity values should be used, not Acceptable Daily Intake (ADI) values (IPCS 1995), which assume lifetime exposure. For this purpose minimum lethal dose estimates of lead (IPCS, 1994) can be compared to the amount of lead a person may be exposed to if they ingested contaminated material in a relatively short period of time (from within 1 day to 14 days). A lethal dose rate for lead is approximately **500 mg** of absorbed lead for an adult. In order to carry out a risk assessment, which itself considers different bioavailabilities, the absorbed dose value is used, i.e. 500 mg for an adult and an equivalent dose 100 mg is used for child. The exposed dose can be calculated by Equation [2] using the highest Pb concentration of 41900 mg/kg in the soil and 25% absolute bioavailability (ABA).

Equation [2]:

 $Dose_{exposed} = C_{soil} xABA\%$

Dose_{exposed} = 41900 mg/kg x 25% = 10475 mg/kg

Hence, the effective concentration of Pb in soil is 10475 mg/kg. To give a lethal dose of 500 mg absorbed Pb for an adult it will require 0.0477 kg (47.7 g, i.e. 500 mg divided by 10475 mg/kg) of soil. To give a lethal dose of 100 mg absorbed Pb for a child it will require 0.0095 kg (9.5 g) soil.

It can be concluded that based on a worst case scenario, the highest soil lead of 41,900 mg/kg coupled with the highest bioaccessibility of 25% the dose, in terms of amount of soil required to be ingested to cause acute poisoning in an adult is 47.7 g and in a child is 9.5 g.

The results from a number of different scenarios are shown in Table 12. It must be noted also that bioavailability (Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007) is general much lower than the more conservative estimate of potential uptake using bioaccessibility data, and hence the toxicity here is likely to be being overestimated.

When considering sub-chronic exposure, i.e. for one to three months (Eaton and Gilbert, 2008), another suitable threshold level must be chosen for comparison with the exposure scenarios for this site. The Lowest Observable Adverse Effect (LOAEL) in human volunteers is 0.2 mg/kg/day (14 mg/day, adults; 2.8 mg/day, child) of lead acetate for a duration of 21 days (IPCS, 1994). Hence, all the exposure values in Table 12 are lower than the dose rate known to cause sub chronic effects for adults. Exposure scenarios for children exposed to soil with the highest lead concentration, for example 40,000 mg/kg, combined with bioavailabilities of >90% (an unlikely scenario), the sub-chronic dose rate will be

exceeded (not shown in Table 12 because it is extremely unlikely that the bioavailability of lead in Leichhardt River samples would be greater than 25%).

Dust suspended in the air is likely to be relatively small compared to soil as a source for oral ingestion route of exposure. Therefore Pb in air is considered to be insignificant in this context. Furthermore, dust inhalation as a route of exposure has been discussed in Section 4.1.2.

It is concluded that both acute and sub chronic toxicities caused by contaminated soil are unlikely.

Table 12: Estimated lead intake (mg absorbed) by a 70 kg adult and a 14 kg child assuming a soil ingestion rate of 25 mg and 100 mg respectively for soil pathway only.

Acute & Sub chro	Acute & Sub chronic Lead – Soil						
	NEPM	NEPM	NEPM	>NEPM	>NEPM	>NEPM	
Pb (mg/kg)	HIL A	HIL E	HIL D	HIL F	HIL F	HIL F	
	300	600	1200	2400	6000	40000	
Adult							
ABA=25%	0.00188	0.00375	0.00750	0.01500	0.03750	0.22	
ABA=20%	0.00150	0.00300	0.00600	0.01200	0.03000	0.2	
ABA=10%	0.00075	0.00150	0.00300	0.00600	0.01500	0.1	
ABA=2.0%	0.00015	0.00075	0.00060	0.00120	0.00300	0.02	
Child							
ABA=25%	0.0075	0.0150	0.0300	0.0600	0.1500	0.875	
ABA=20 %	0.0060	0.0120	0.0240	0.0480	0.1200	0.8	
ABA=10%	0.0030	0.0060	0.0120	0.0240	0.0600	0.4	
ABA=2.0%	0.0005	0.0012	0.0024	0.0048	0.0120	0.08	
LEGEND:							
	Lead value	= NEPM HIL	'A' (Standard	residential w	vith garden)		
	Lead value	= NEPM HIL	'E' (Parks, re	creational, pl	aying fields)		
	Lead value	= NEPM H	IIL 'D' (Resid	dential with	minimal soil		
	access)						
	Lead value	e > NEPM I	HIL 'F' (Con	nmercial/Indu	strial: 1500		
	mg/kg)						
Cells in red - Estimated ingestion value for lead exceeding minimum acute (24 hrs)							
lethal dose rate (a single dose of 500 mg Pb absorbed for an adult; 100 mg Pb							
absorbed for a chil							
Available fraction	of soil lead	(e.g. Absolut	te Bioavailab	IIITY) ABA =			
absolute bioavalla	onity						

NB: an absence of cells in red indicates the exposure is less than the ADI.

4.1.3.2 Chronic Exposure

Chronic exposure refers to an exposure period of 365 days or more (ATSDR, 1999). The health-based investigation threshold of the Provisional Tolerable Weekly Intake (PTWI) for exposure of lead, established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), is 25 μ g Pb/kg body weight (IPCS, 1995).

For a 70 kg adult, the acceptable daily intake (ADI) of lead is **0.25 mg** (250 μ g). Similarly, for a child weighing 14 kg, the ADI is **0.05 mg** (50 μ g).

The NHMRC drinking guideline value of 0.01 mg/L for lead in Australia has been derived based on this ADI value (ADWG, 2004). NEPMs (National Environmental Protection Measures) are set based on a default of 100% bioavailability (NEPC, 1999). When bioavailability data is available, a more accurate estimate of the exposure can then be calculated.

A generally accepted but conservative figure for daily soil ingestion for the age group 1-5 years (with an average body weight of 14 kg) is 100 mg/day (Taylor, 1991). There appears to be virtually no published data enabling quantification of adult soil ingestion. A tentative estimate of 50 mg/kg from a pilot investigation of six adults, however, has been made (Calabrese *et al.*, 1989). Paustenbach (1989) claimed the figure of 2-5 mg/day was more reasonable and justifiable based upon his review of the literature and the belief that adults ingest about one-tenth the amount of soil ingested by children (Paustenbach, 1989). For the current situation, a conservative intake of 25 mg (0.000025 kg) per day ingested via hand-to-mouth activities for adults under residential conditions has been used.

Whilst the actual contribution of soil from a contaminated site is likely to be only a proportion of that ingested, for the purpose of risk assessment, it can be assumed that the contaminated site contributes 100% to soil ingested.

The exposure of lead to an adult by soil ingestion can be calculated using the following Equation 3.

Equation [3]:

Pb_{(SI)adult}= Pb_{(C)soil} x 0.000025 x ABA%

Where:

 $Pb_{(SI)adult}$ = lead (mg) via soil ingestion per day $Pb_{(C)soil}$ = lead concentration (mg/kg) of soil ABA% = absolute bioavailability (%) 0.000025 = soil (kg) ingested by a 70 kg body weight (b.w.) adult per day Similarly, the exposure of lead to a child by soil ingestion can be calculated using Equation 4.

Equation [4]:

 $Pb_{(SI)child} = Pb_{(C)soil} \times 0.0001 \times ABA\%$

Where:

 $Pb_{(SI)child}$ = lead (mg) via soil ingestion per day $Pb_{(C)soil}$ = lead concentration (mg/kg) of soil ABA% = absolute bioavailability (%) 0.0001 = soil (kg) ingested by a 14 kg b.w. child per day

Table 13 represents the likelihood of lead exposure from soil exceeding the ADI.

To ensure that all exposure pathways are taken into consideration the lead exposure is combined with realistic estimates of food (IPCS, 1995) and water lead intake for an Australian adult (70 kg) and child (14 kg). Estimates of lead (see IPCS, 1995, p92) absorbed by adults and children from food are 10 μ g/day (0.01 mg/day) and 25 μ g/day (0.025 mg/day), respectively, based on 10% bioavailability in adults and 50% bioavailability (conservative estimate) in children. Whereas the corresponding estimates of lead absorbed by adults and children from drinking are 2 μ g/day (0.002 mg/day) and 5 μ g/day (0.005 mg/day), respectively. The estimates of lead intake from water are in agreement with the calculation based on current Australian drinking water guideline value (0.01 mg/L) (NHMRC, 2004). For water, a daily consumption of 2 L for adults and 0.5 L for a child (14 kg) is used when calculating lead exposure, assuming 10% bioavailability as suggested by IPCS expert task group (IPCS, 1995).

Equation 5 provides an overall estimate of absorbed lead from sources including soil, food and water.

Equation [5]:

 $Pb_{(SI)}$ = [$Pb_{(C)soil}$ x Ingestion_{soil} x ABA%] + Pb_{food} + Pb_{water}

Total Intake = Soil + Food + Water

Where: $Pb_{(SI)} = lead (mg)$ via soil ingestion per day $Pb_{(C)soil} = lead concentration (mg/kg) of soil$ Ingestion_{soil} = 25 mg (0.0000 25kg) for an adult; 100 mg (0.0001kg) for a child $Pb_{food} = 10 \ \mu g/day (0.01 \ mg/day)$ for an adult; 25 $\mu g/day (0.025 \ mg/day)$ for a child $Pb_{water} = 2 \ \mu g/day (0.002 \ mg/day)$ for an adult; 5 $\mu g/day (0.005 \ mg/day)$ for a child The calculated intake does not exceed the ADI for lead when food and water are included for an adult (Table 13). In the case of a child, lead from food and water from normal sources contribute to significant intake of the daily exposure (Table 13). Only when coupled with the very high Pb concentration of 40,000 mg/kg in the soil can an ABA of 2% result in exposure exceeding the ADI in children.

Chronic Lead Exposure- Soil						
	NEPM	NEPM	NEPM	>NEPM	>NEPM	>NEPM
	HIL A	HIL E	HIL D	HIL F	HIL F	HIL F
Pb (mg/kg)	300	600	1200	2400	6000	40000
Adult						
ABA=25%	0.00188	0.00375	0.00750	0.01500	0.03750	0.21875
ABA=20%	0.00150	0.00300	0.00600	0.01200	0.03000	0.2
ABA=10%	0.00075	0.00150	0.00300	0.00600	0.01500	0.1
ABA=2.0 %	0.00015	0.00030	0.00060	0.00120	0.00300	0.02
Child						
ABA=25%	0.0075	0.0150	0.0300	0.0600	0.1500	0.875
ABA=20%	0.0060	0.0120	0.0240	0.0480	0.1200	0.8
ABA=10%	0.0030	0.0060	0.0120	0.0240	0.0600	0.4
ABA=2.0%	0.0006	0.0012	0.0024	0.0048	0.0120	0.08
Chronic Lead Expo	osure- Soil +	Food + Wate	r			
Adult						
ABA=25%	0.1388	0.01575	0.1950	0.027	0.0495	0.23075
ABA=20%	0.0135	0.015	0.018	0.024	0.042	0.212
ABA=10%	0.01275	0.0135	0.015	0.018	0.027	0.112
ABA=2.0%	0.01215	0.0123	0.0126	0.0132	0.015	0.032
Child						
ABA=25%	0.0375	0.045	0.060	0.090	0.180	0.905
ABA=20%	0.036	0.042	0.054	0.078	0.15	0.812
ABA=10%	0.033	0.036	0.042	0.054	0.09	0.412
ABA=2.0%	0.0306	0.0312	0.0324	0.0348	0.042	0.092
LEGEND:		<u></u>				-
	Lead value	= NEPM HIL	'A' (Standard	residential w	/ith garden)	
	Lead value	= NEPM HIL	'E' (Parks, re	creational, pla	aying fields)	
	Lead value	= NEPM H	IIL 'D' (Resid	dential with r	minimal soil	
	access)					
	Lead va	alue >	NEPM	HIL 'F'		
Rod Colle Estima	(Commercia	al/industrial: 1	d oxecode Al			
Red Cells - Estimated Ingestion value for lead exceeds ADI (mg)						
Bioavailability)		.au (c.g. 0	.1 – 10 /	Absolute		
Adult (70 kg) subje	ect has ADI of	f 0.25 mg of l	ead (WHO, 1	989)		
Child (14 kg) subject has ADI of 0.05 mg of lead (WHO, 1989)						

Table 13: Estimated daily lead intake (mg/day) by a 70 kg adult and a 14 kg child; firstly for ingestion of soil only, and secondly for soil + food + water.

However, when ABA is 10% (although unlikely for contaminated soil) then a soil Pb concentration of <2,400 mg/kg is recommended; and when ABA is 20% or higher then a soil Pb concentration of <1200 mg/kg is recommended.

Exposure to Pb from home-grown produce has not been incorporated into the daily intake calculation. Although some broad leaf vegetables and root crops had been identified to have contained elevated levels of Pb from a limited survey conducted in Mount Isa by the Government Chemical Laboratory and the Division of Environmental Health and Occupational Health (Sadler *et al.*, 1990), the data set is old and may not reflect the current situation of dust deposition rate. More importantly, home-grown produce was not found to be a significant pathway for Pb exposure in a more recent health survey (Queensland Health 2008) which assessed the home environment, including food growing, within the homes of children identified as having elevated blood lead levels. The relatively infrequent consumption of home-grown fruits and vegetables is unlikely to significantly contribute to the ADI. As part of routine hygiene practices, it is suggested that home-grown fruits and vegetables should be washed before consumption to remove dust, soil and bacteria.

It is concluded that chronic Pb poisoning is not likely in adults. However, high Pb in the soil (>2,400 mg/kg) could result in Pb exposure exceeding the average daily intake in young children if the absolute bioavailability of Pb is greater than 10%. Similarly, a soil Pb of >1200 mg/kg could result in Pb exposure exceeding the ADI in young children if the ABA of Pb is greater than 20%. This conclusion is most relevant to residences where children spend a high frequency of their time.

4.2 Arsenic Exposure Pathways and Subsequent Risk Calculations

As with the health risk assessment for lead, the risk assessment for arsenic investigates the significance of the three potential exposure pathways to humans, namely dermal, inhalation/ingestion and oral exposure.

4.2.1 Dermal Exposure

A number of studies have been conducted to investigate dermal absorption of arsenic (Boutwell, 1963; Kurokawa *et al.*, 1989; Wahlberg *et al.*, 1896; Wester *et al.*, 1993). These studies indicate that direct dermal contact with arsenic may be of concern at high exposure levels if arsenic is in a soluble form. For low levels of dermal exposure, arsenic is unlikely to cause any significant irritation. There are no studies that link dermal exposure with arsenic to cancer in humans.

At the IPCS Task Group meeting on arsenic and arsenic compounds held in Brisbane (November, 1999), the Task Group concluded that dermal exposure is

not a significant pathway in human health risk assessment (IPCS 2001). The dermal absorption rate is generally less than 1% of the dose (Wester *et al.*, 1993).

Hence, the dermal exposure of arsenic by this route is probably insignificant in the context of this risk assessment and is not considered further.

4.2.2 Dust Inhalation/Ingestion

As with lead, the inhalation of dust containing arsenic is an important consideration in the occupational environment (WHO, 1995). Larger particles will eventually be swallowed while smaller particles may also be absorbed directly into the lymphatics from the lungs.

The exposure route of arsenic via inhalation is not considered to be a significant problem in residential settings. Most available data related to human inhalation of arsenic derive from occupational settings such as smelters and chemical plants, where the predominant form of airborne arsenic is arsenic trioxide dust. In recent times, inhalation of arsenic causing chronic arsenicosis in humans has been reported in Guizhou, south-western of Peoples Republic of China, where arsenic contaminated coal is used for cooking, drying of food crops and for heating purposes (Shraim *et al.*, 2003). Even in such an extreme case, the inhalation route of exposure is still the minor pathway. The major route of exposure is believed to be via the ingestion of arsenic-dust deposited on food.

In Australia, the National Research Centre for Environmental Toxicology (EnTox) has conducted dust samplings around houses built on contaminated land with arsenic of natural origin (Ng *et al.*, 1998; Ng, 1999). The highest arsenic containing dusts were usually found in "heavy traffic" areas of houses, such as hallways and doorways. The highest concentration of arsenic found in dust was 434 mg/kg from houses with soil concentrations ranging from 32 to 1597 mg/kg (Ng *et al.*, 1998; Ng, 1999).

The following calculation is used to determine if elevated levels of arsenic in soil contribute a significant source of arsenic by inhalation. The calculation (Ng, 1999) is a worst case scenario; that airborne dust has the same composition at the highest arsenic concentration (Table 6) of 541 mg/kg, and that people are breathing in this dust eight hours a day five days a week.

The following guidelines are used as basis of the calculation:

 The recommended allowable house dust particle level (indoor air total suspended particulates) in the indoor air is 90 μg/m³ (90 x 10⁻⁶ g/m³) according to the Interim National Indoor Air Quality Goal Recommended by NHMRC (NHMRC, 1990); and

 Time-weighted average (TWA) concentration of arsenic (as arsenic and its soluble compounds) over an eight-hour working day, for a five-day working week has been set at 0.05 mg/m³ (50 μg/m³) for the occupational environment (Worksafe Australia, 1995).

These two assumptions are applicable to residential occupancy where adults and children may be located on a continuous basis.

The calculation is based on the assumption that the dust level is at the highest amount of 90 μ g/m³ (90 x 10⁻⁶ g/m³), as indicated above. If the highest arsenic concentration in the soil / dust was 541 mg/kg (μ g/g), the arsenic level in the air (As_{air}) at the site of specified soil concentration is calculated using the equation below.

Equation [6]:

As_{air} = Soil concentration (mg/kg) x Recommended allowable dust level (90 x 10^{-6} g/m³ NH&MRC 1990) = Concentration in air (µg/m³)

$$As_{air} = 541 \text{ mg/kg x } 90 \text{x} 10^{-6} \text{ g/m}^3 = 0.04869 \ \mu\text{g/m}^3$$

The TWA safety factor (SF) (Worksafe Australia 1995) can then be applied to determine the likelihood of influence.

SF = (50 μg/m³)/ 0.04869 μg/m³ = **1027**

Based on the above assumptions, the dust in air directly derived from the source of the highest concentration of arsenic sampled, would be 1027 times below the recommended TWA value for occupational exposure of arsenic. The above risk assessment for the soil is conservative, since one assumes the worst case scenario. These calculations are based on 100% pulmonary bioavailability, and assume that concentration of arsenic in dust is the same as concentration of arsenic in a single source. Hence it is anticipated that the exposure and the uptake could be expected to be significantly reduced.

One would expect the dust level at the residential area is lower than that of the occupational setting. However, if the assumption is made that the high dust level is the same in the residential area and that some residents (e.g. home-bound people, young infants and recent mothers) are exposed to the same arsenic level 24 hours of a day the safety factor will be 3 fold less than that calculated above. This still amounts to a safety factor of about 330 assuming the highest air-borne soil arsenic (As_{air}) is 541 mg/kg at the specific site. The exposure and the risk are reduced even further in areas that are recreational rather than residential.

Therefore, the highest arsenic contamination level in soil identified (541 mg/kg) is not considered to be hazardous to the potential residents via inhalation alone. Having said this, during periods of airborne dust creation, such as earth moving,

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

personal precautionary measures can be used, as in any dusty environment, to reduce exposure even further.

4.2.3 Oral Exposure

It should be noted that arsenic in water is about 80-98% bioavailable for absorption via the oral route. The bioavailability from soil is much less than that of water. For mineral based waste materials the absolute bioavailability (ABA) of arsenic-contaminated soil is likely to be less than 10% (Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007). For a conservative estimate, an ABA of up to 25% is employed here for illustration purposes.

4.2.3.1 Acute and Sub Chronic Exposure

The minimum lethal dose of arsenic (ATSDR, 2000) can be used to determine acute exposure risks, by comparing it to the amount of arsenic a person may be exposed to if they ingested mine waste material from a contaminated site during a 1 to 14 day exposure period. A commonly used lethal dose rate for arsenic is 1-3 mg/kg body weight (70-210 mg/day of arsenic for a 70 kg adult; 14 - 42 mg/day for 14 kg child) (Vallee *et al.*, 1960).

The calculation is made based on the highest concentration of As identified in the sampling program of 541 mg/kg (i.e. C_{soil}) and the highest ABA of 25% The calculated dose is shown in Equation 7.

Equation [7]:

Dose_{exposed}= C_{soil} x ABA%

Dose_{exposed}=541mg/kg x 25%=135 mg/kg

Hence, the effective arsenic concentration is 135 mg/kg (e.g. 1/4 of the original concentration). So the amount of soil needed to acutely poison an adult person (70 kg body weight) is 0.518 kg to 1.555 kg; and 0.104 kg to 0.311 kg to acutely poison a child. The results from a range of scenarios are presented in Table 14.

It can be concluded that the arsenic in soil is very unlikely to cause acute toxicity in humans because people are not likely to ingest such large amounts of soil under normal circumstances. **Table 14:** Estimated daily arsenic intake (mg/day) by a 70 kg adult and a 14 kg child assuming a soil ingestion rate of 25 mg and 100 mg, respectively, for soil pathway only.

	Acute & Su	bchronic Arse	enic - Soil			
	NEPM	NEPM	NEPM	> NEPM	> NEPM	>NEPM
As (mg/kg)	HIL A	HIL E	HIL D	HIL F	HIL F	HIL F
	100	200	400	800	2000	10000
	Adult					
ABA=25%	0.00063	0.00125	0.00250	0.00500	0.01250	0.06250
ABA=20%	0.00050	0.00100	0.00200	0.00400	0.01000	0.05000
ABA=10%	0.00025	0.00050	0.00100	0.00200	0.00500	0.02500
ABA=2%	0.00005	0.00010	0.00020	0.00040	0.00100	0.00500
	Child					
ABA=25%	0.0025	0.0050	0.0100	0.0200	0.0500	0.2500
ABA=20%	0.0020	0.0040	0.0080	0.0160	0.0400	0.2000
ABA=10%	0.0010	0.0020	0.0040	0.0080	0.0200	0.1000
ABA=2%	0.0002	0.0004	0.0008	0.0016	0.0040	0.0500
LEGEND:						
	Arsenic valu	ue = NEPM H	IIL 'A' (Stand	ard residentia	al with garde	ר)
	Arsenic valu	ue = NEPM H	IIL 'E' (Parks	, recreational	, playing field	ls)
	Arsenic valu	ue = NEPM ⊦	IIL 'D' (Resid	ential with mi	inimal soil ac	cess)
	Arsenic valu	ue > NEPM ⊦	IIL 'F' (Comm	nercial/Indust	rial: 500 mg/l	<g)< td=""></g)<>
Red Cells - Estim	ated ingestic	on value for	arsenic exce	eding minim	um acute (24	hrs) lethal
dose rate (70 mg/	day, adult; 14	mg/day, chil	d)			
Estimated ingestic	Estimated ingestion value for arsenic exceeding dose rate known to cause subchronic (up to					
three months) health effects (7 mg/day, adult; 1.4 mg/day, child)						
Available fraction	of soil arsenio	c (e.g. ABA =	= 2, 10, 20 &	25%)		
Adult (70 kg) subje	ect with avera	age daily soil	ingestion of 2	25 mg		
Child (14 kg) subje	ect has daily	soil ingestion	of 100 mg			

NB : an absence of cells in red indicates the exposure is less than the ADI.

When considering an exposure period of up to 3 months (as a once-off exposure), the most appropriate exposure classification is sub-chronic exposure, i.e. one to three months (Eaton and Gilbert, 2008). Therefore, another suitable threshold level must be chosen for comparison with the exposure scenarios for this site, rather than the ADI. Deciding on such a threshold value is difficult, as little information exists regarding sub-chronic doses in humans. However, a dose of approximately 7 mg/day (assuming adult subject) of arsenic in water for a duration of three months is reported as causing severe nausea, diarrhea, pain, cramps, vomiting, and blood in the faeces (ATSDR, 2000). The relative dose for a child would be 1.4 mg/day. Hence, all the exposure values in Table 14 are below the dose rate known to cause sub-chronic effects for both adults and children, respectively.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

4.2.3.2 Chronic Exposure

Chronic exposure is defined as a repeated dose for a period of three months or greater (e.g. lifetime exposure) (Eaton and Gilbert, 2008). The health-based investigation threshold of the Tolerable Weekly Intake (TWI) for exposure of arsenic, established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), is 0.015 mg As/kg body weight (WHO, 1989). Hence, for a 70 kg adult, the Acceptable Daily Intake (ADI) threshold of arsenic is **0.15 mg** (150 μ g). Similarly, for a child weighing 14 kg, the ADI is **0.03 mg** (30 μ g).

As discussed in the health risk assessment for lead, the daily soil ingestion is taken to be 100mg/day for the 1-5 year age group and 25mg/day for adults under residential conditions. Whilst the actual contribution of soil from a contaminated site is likely to be only a proportion of that ingested, for the purpose of risk assessment, it can be assumed that the contaminated site contributes 100% to soil ingested.

The exposure of arsenic to an adult by soil ingestion can be calculated using the following Equation 8.

Equation [8]:

 $As_{(SI)adult} = As_{(C)soil} \times 0.000025 \times ABA\%$

Where:

 $As_{(SI)adult}$ = arsenic (mg) soil ingestion by an adult per day $As_{(C)soil}$ = arsenic concentration (mg/kg) of soil 0.000025 = soil (kg) ingested by a 70 kg adult per day ABA% = absolute bioavailability (%)

Similarly, the exposure of arsenic to a child by soil ingestion can be calculated using Equation 9.

Equation [9]:

 $As_{(SI)child} = As_{(C)soil} \times 0.0001 \times ABA\%$

Where:

 $As_{(SI)soil}$ = arsenic (mg) via soil ingestion by a child per day $As_{(C)soil}$ = arsenic concentration (mg/kg) of soil ABA% = absolute bioavailability (%) 0.0001 = soil (kg) ingested by a 14 kg b.w. child per day Water not applicable here until Equation 10 (see below)

The potential arsenic exposure via ingestion of soil can thus be calculated according to site-specific data including arsenic concentration of each soil and its bioavailability (see Table 15). The calculated results can then be compared to the ADI (i.e. 0.15 mg and 0.03 mg of arsenic for adults and children, respectively) as recommended by WHO (1989).

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

To ensure that all exposure pathways are taken into consideration, the arsenic exposure is combined with realistic estimates of food (IPCS, 1995) and water arsenic exposure for an Australian adult (70 kg) and child (14 kg). Food exposure estimates from arsenic are taken directly from the International Programme on Chemical Safety (IPCS, 2001) literature expressed in mg/kg, assuming 100% bioavailability. Note, only 25% of the total estimated intake for adults and children in Australia are used, to take into account the relatively high proportion of organic arsenic in the diet (IPCS, 2001). Estimates of arsenic in drinking water vary markedly across the country, and therefore daily intake was calculated by combining estimates of daily water consumption with the Australian drinking water guideline value (0.007 mg/L) (ADWG, 2004). For water, a daily consumption of 2 L for adults and 0.5 L for a child (14 kg) is used when calculating arsenic ingestion, assuming 100% bioavailability. This estimate provides a worst-case scenario of arsenic exposure where site-specific water values are not available and is calculated as Equation 10.

Equation [10]:

 $As_{(W)adult} = As_{(C)} \times L_{(adult)} \times ABA\%$

Where

 $As_{(W)adult}$ = arsenic intake by an adult from water $As_{(C)}$ = water concentration of arsenic (i.e. Australian guideline, 0.007 mg/L (ADWG 2004)) $L_{(adult)}$ = adult consumption of drinking water per day in litres ABA% = absolute bioavailability, assumed to be 100% for water

Therefore, the total intake of arsenic by an adult by ingestion of soil, food and water can be calculated using the following Equation 11. The soil concentration range for arsenic is based on the information provided.

Equation [11]: As_{(SI)adult}= [As_{(C)soil} x 0.000025AB%] + As_{(C)food} x ABA% + As_{(C)water} x ABA%

Total intake = Soil + Food + Water

Where:

 $\begin{array}{l} As_{(SI)adult} = arsenic \ (mg) \ via \ soil \ ingestion \ per \ day \\ As_{(C)soil} = arsenic \ concentration \ (mg/kg) \ of \ soil \\ 0.000025 = soil \ (kg) \ ingested \ by \ a \ 70 \ kg \ adult \ per \ day \\ ABA\% = absolute \ bioavailability \ (\%) \\ As_{(C)food} = arsenic \ (mg) \ via \ food \ ingestion \ per \ day \ for \ average \ Australian \\ \end{array}$

Chronic Arsenic Exposure - Soil						
	NEPM	NEPM	NEPM	>NEPM	>NEPM	>NEPM
Ac (ma/ka)	HIL A	HIL E	HIL D		HIL F	HIL F
AS (IIIg/Kg)	100	200	400	800	2000	10000
Adult	0.00000	0.00405	0.00050	0.00500	0.04050	0.00050
ABA=25%	0.00063	0.00125	0.00250	0.00500	0.01250	0.06250
ABA=20%	0.00050	0.00100	0.00200	0.00400	0.01000	0.05000
ABA=10%	0.00025	0.00050	0.00100	0.00200	0.00500	0.02500
ABA=2%	0.00005	0.00010	0.00020	0.00040	0.00100	0.00500
Child						
ABA=25%	0.0025	0.0050	0.0100	0.0200	0.0500	0.2500
ABA=20%	0.0020	0.0040	0.0080	0.0160	0.0400	0.2000
ABA=10%	0.0010	0.0020	0.0040	0.0080	0.0200	0.1000
ABA=2%	0.0002	0.0004	0.0008	0.0016	0.0040	0.0500
Chronic Arsenic E	xposure- Soi	I + Food + W	ater			
Adult						
ABA=25%	0.03038	0.03100	0.03225	0.03475	0.04225	0.09225
ABA=20%	0.03025	0.03075	0.03175	0.03375	0.03975	0.07975
ABA=10%	0.03000	0.03025	0.03075	0.03175	0.03475	0.05475
ABA=2%	0.0298	0.02985	0.02995	0.03015	0.03075	0.03475
Child						
ABA=25%	0.0103	0.0128	0.0178	0.0278	0.0578	0.2578
ABA=20%	0.0098	0.0118	0.0158	0.0238	0.0478	0.2078
ABA=10%	0.0088	0.0098	0.0118	0.0158	0.0278	0.1078
ABA=2%	0.0080	0.0082	0.0086	0.0094	0.0118	0.0578
LEGEND:	-	-	-	-	-	
	Arsenic valu	ue = NEPM H	IL 'A' (Stand	ard residentia	al with garde	n)
	Arsenic valu	ue = NEPM H	IIL 'E' (Parks	, recreational	, playing field	ls)
	Arsenic valu	ue = NEPM H	IIL 'D' (Resid	ential with mi	inimal soil ac	cess)
	Arsenic valu	ue > NEPM H	IIL 'F' (Comm	nercial/Indust	rial: 500 mg/l	<g)< td=""></g)<>
Red Cells- Estima	ted ingestion	value for ars	enic exceeds	s ADI (mg)		
Available fraction	of soil arsenie	c (e.g. ABA =	2, 10, 20 & 2	25%)		
Adult (70 kg) subje	ect has ADI o	of 0.15 mg of	arsenic (IPC	S, 2001)		
Child (14 kg) subject has ADI of 0.03 mg of arsenic (IPCS, 2001)						

Table 15: Estimated daily arsenic intake (mg/day) by a 70 kg adult and a 14 kg child assuming a soil ingestion rate of 25 mg and 100 mg, respectively.

Once food and water are taken into consideration in the diet where soil arsenic greater than 2000 mg/kg and the ABA is 20% or higher there is a potential risk for exceeding the ADI in children. When soil arsenic is greater than 10000 mg/kg and the ABA is 2% or higher there is a potential risk for exceeding the ADI in children. This table shows that for soil arsenic < 600 mg/kg there is no risk.

Whilst there is an increase in the calculated exposure as a result of the inclusion of potential intake of arsenic via food and arsenic it is not significant and does not

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

increase the number of concentration /bioavailability combinations which exceed the ADI (Table 15). Regardless of whether food and water are taken into consideration, soil arsenic > 2000 mg/kg combined with an ABA of 20% or higher there is a potential risk for exceeding the ADI in children (Table 15). When soil arsenic is > 10000 mg/kg and the ABA is 2% or higher there is a potential risk for exceeding the ADI in children. This table shows that for soil arsenic < 600 mg/kg there is no risk. It is noted that at the lower soil arsenic concentration the inclusion of food and water contributions does significantly increase the exposure, however not to the point it exceeds the ADI.

From Tables 14-15 for arsenic, it could be concluded that arsenic levels found in the Phase 1 study samples would not constitute either acute or chronic health risk to adults or children given that the highest concentration was 541 mg/kg (L13 soil). The actual bioaccessibility of arsenic in this soil sample was 1%. The bioaccessibility of all samples collected was less than 25%. Thus, it can be concluded that there is no significant risk associated with arsenic.

5. DISCUSSION

In order to assess the residual impact of historical pollution within the river and the potential for human and ecological impacts, the sample analysis results are compared against the NEPM Health Investigation (HIL) Level E soil guidelines (NEPC 1999) and ANZECC (2000) sediment ISQG guidelines (Table 2).

Further, the investigation applies bioaccessibility data to the results to allow for site specific risk assessment.

Risk to human and ecological health is assessed through the integration of the total concentration data, bioaccessibility adjusted concentration data, sediment extraction data and toxicity results and the desktop human health risk assessment in order to understand areas of concern requiring further attention.

5.1 Comparison of soil concentrations with NEPM HILs and EILs

Initially, the total concentrations of soils and sediments are compared against the NEPM HIL Level E. The sample sites exceeding HIL Level E for the various metals and metalloids are listed in Table 16. This comparison with the respective HILs assumes that the bioavailability is 100%.

Sites L4-L6 at the swimming pool and downstream Leichhardt River Sites (L14-L16) did not trigger any exceedances of the HIL Level E, and no further investigation is required at these sites.

Results from Sites L4, L5 and L6, are the only urban soil samples, and hence are the only samples which are able to be compared against the Ecological Investigation Level (EILs - Interim Urban) for phytotoxicity. Comparison at these sites shows that there are slight exceedances for cadmium at Site L5 and for zinc at Sites L5 and L6 but not for any other combination of metal or metalloid. There was no visible evidence of affected plants or grass. Given the land use at the location as being recreational and the lack of visible impact, it is determined not to be of concern and no further assessment is required.

Metal/Metalloid	HIL Level E	Site exceeding HIL Level E (Total Concentration)	Sites exceeding HIL Level E (BAc adjusted concentration)
Arsenic	200	L2 (198 mg/kg) L3 (207.3 mg/kg) L8 (479.6 mg/kg) L10 (247.2 mg/kg) L11 (396.7 mg/kg) L13 (541.2 mg/kg)	Nil
Cadmium	40	L8 (137.3 mg/kg) L13 (185.5 mg/kg)	L8 (52.2 mg/kg), L13 (65.0 mg/kg)
Cobalt	200	L11 (247.1 mg/kg)	Nil
Copper	2000	L2 (4,095.6 mg/kg) L3 (4,380.4 mg/kg) L11 (10,873.8 mg/kg)	L3 (2,015 mg/kg), L11 (2,718 mg/kg)
Nickel	600	Nil	Nil
Lead	600	L2 (2,171.8 mg/kg) L3 (2,462.8 mg/kg) L8 (25,009.8 mg/kg) L10 (6,601.2 mg/kg) L11 (6,710.4 mg/kg) L13 (41,886.4 mg/kg)	L8 (4,002 mg/kg), L10 (1,122 mg/kg), L11 (1,074 mg/kg), L13 (10,053 mg/kg)
Zinc	14000	L8 (49,382 mg/kg) L13 (30,235.7 mg/kg)	L8 (17,284 mg/kg)

Table 16 Summary of soil samples exceeding NEPM HIL Level E for both total concentrations and bioaccessibility adjusted concentrations.

The procedure when the NEPM HIL is exceeded by total concentrations is to undertake a toxicological appraisal for the purpose of hazard identification (NEPC 1999), as a means of providing a more accurate estimate of bioavailability of the metal or metalloid. Whilst the NEPM soil guidelines assume 100% bioavailability, this has been shown to be generally not the case with mine waste and mineralised material (Bruce *et al.,* 2007; Diacomanolis *et al.,* 2007), as only a proportion of the mineralised forms of metals and metalloids are potentially soluble in the stomach and intestinal phases.

Bioaccessibility has been demonstrated to give a reliable estimate of bioavailability for both arsenic and lead. In the case of cadmium, copper, nickel and zinc, bioaccessibility is considered to be the best available estimate of bioavailability to apply in this situation.

The bioaccessibility adjusted concentrations can then be re-compared with the NEPM HIL Level E as site-specific criteria (Table 16) which more accurately indicates the significance of the metal/metalloids as health risks in the context of recreational exposure.

The results in Table 16 show that the number of sites / element combinations considered to be potentially significant with respect to human health, in the recreational context, is greatly reduced by factoring in bioaccessibility. Figure 7 shows the various sites where bioaccessibility adjusted concentrations of metals/metalloids continue to exceed HIL Level E and as a result are considered to be contaminated with respect to human health

It is noted that the highest soil lead concentration of 41,900 mg/kg also has the highest bioaccessibility (BAc%) of 25% for Pb. A range of other concentrations (293 – 19,990 mg/kg) had similar BAc% (20-25%).

Although sediment concentrations are not generally compared against the NEPM Soil Guidelines, due to the exceptionally high levels of lead at L12 (sediment) its bioaccessibility adjusted concentrations were compared with HIL Level E guideline. As shown in Figure 7, cadmium, copper and lead were exceeded at L12 as a human health risk for recreational conditions. However, it must be noted that the comparison of <63 μ m fraction sediment data with soil <2 mm fraction is more conservative as the finer fraction of sediment usually has higher metal concentrations, and hence the significance of heavy metal concentrations at L12 to human health is exaggerated by this comparison.

All sites shown in Figure 7 require further action either in the form of additional investigation and/or remediation.



Figure 7: Summary of sites that exceed NEPM Health Investigation Level E when bioaccessibility factors (Table 6) are applied to total concentration data. Each point is labelled with the metals which are in exceedances at that location, i.e. cadmium, copper, lead and zinc.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

5.2 Assessment against the sediment ISQGs

The results from the total concentrations of metals and metalloids and sediment extraction with 1M HCI (Table 17) are interpreted against the ANZECC (2000) ISQG guidelines for sediments (Table 2) in order to assess potential biological effects. A comparison of total concentrations with the ISQG-Low and High trigger values is given in Table 17 and shows that all sites exceeded the Low trigger value and most, excluding the upper and lower sites on the Leichhardt River, the High trigger value, and hence require further investigation. The upper site on the Leichhardt River, L1, is above mining impact and is probably influenced by the presence of natural mineralisation in the fluvial channel.

A lesser number of sites exceed the ISQG-Low trigger values when compared against the 1M hydrochloric acid extract concentrations indicating possible factors controlling bioavailability. Included is Site L1 which shows that extraction with 1M hydrochloric acid does not solubilise metals from mineralised material and requires total digestion. The sites requiring further investigation are L12, which has already been identified as having high total concentrations of heavy metals, L7, L9 and L15, which is a downstream Leichhardt River site.

Metal/metalloid	Sites exceeding ISQG- Low trigger when compared against 1M hydrochloric acid extract	Sites exceeding ISQG- Low trigger when compared against total concentrations	Sites exceeding ISQG-High trigger when compared against total concentrations
Arsenic	Site L12	Sites L7, L9, L12, L15	Sites L7, L12
Cadmium	Sites L9, L12 & L15	Sites L7, L9, L12, L15	Site L12
Cobalt	NA	NA	NA
Copper	Sites L7, L9, L12, & L15	Sites L1, L7, L9, L12, L15, L16	Sites L7, L9, L12, L15
Lead	Sites L7, L9, L12 & L15	Sites L7, L9, L12, L15, L16	Sites L7, L9, L12 & L15
Nickel	Site L7	Sites L1, L7, L9, L12, L15, L16	L7
Antimony	None	Site 12	None
Zinc	Sites L9, L12 &L15	Sites L7, L9, L12, L15	Sites L9, L12, L15

 Table 17:
 Summary of sites that exceed ISQG-Low trigger for sediment

Comparison of the sites exceeding the ANZECC (2000) ISQG-Low guidelines for sediments (Table 17) against the results for aquatic toxicity in Tables 9 and 10 shows that only sediments for the Sites L9 and L12 exhibit significant toxicity as determined from the 10-day whole sediment survival toxicity test using the estuarine amphipod *Corophium spp* and the 48 hour acute (survival) toxicity test using the freshwater cladoceran *Ceriodaphnia cf dubia*.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

While the total lead concentration at Site L12 was significant (20,000 mg/kg in the <63 μ m fraction) it was much lower at L9 (239 mg/kg in the <63 μ m fraction). The metal and arsenic concentrations in the sediment elutriates (Table 11) indicate that the toxicity of the sediments may be directly related to the solubility of those metals and arsenic in the elutriates rather than to any exceedances of the ISQGs for any of the elements studied. The results given in Tables 9 and 10 also show that the downstream Leichhardt River sediments do not exhibit any toxicity to the aquatic test species implying that the ANZECC ISQGs are overestimating toxicity from the mineralisation in the Leichhardt River sediments. This includes Site L1 but excludes Sites L9 and L12 which are clearly of concern in regards to their toxicity and require thorough investigation. In order to understand the influence on endpoint species a more holistic study including aspects such as water quality is required.

5.3 Results for acid potential

Two samples were examined from the east (Site L10) and west (Site L11) sides of the Velodrome in the Leichhardt River to understand their acid generating potential. The material was waste rock which had been placed in that area historically to prevent erosion from impacting on the Velodrome. The results in Table 8 indicate that at Site L10 there is a high acid-producing potential but that the material is only oxidising slowly as the saturated paste test did not show acid pH. At Site L11, tests showed no acid-producing potential and no generation of acid from the saturated paste test. Whilst these materials appear to be in an advanced oxidation stage, it is noted that both these sites had elevated concentrations of heavy metals. Hence, this is an area at which remediation should be considered.

5.4 Significance of metals and metalloids to human health

The results from Table 6 show that elevated concentrations of cadmium, cobalt, copper, lead and zinc occur at some of the sites for soils and sediments. Compared against the NEPM guidelines, the bioaccessibility adjusted concentrations indicate that they may exceed safe levels for human ingestion at some of the sites. In order to better understand the potential risk to human health from elevated lead and arsenic levels within the river soil /sediments, a desktop human risk assessment was undertaken.

Detailed exposure calculations were performed for lead and arsenic, taking into account the three pathways to humans, namely dermal, inhalation/ingestion and oral exposure (Section 4). In general, the most significant pathway for both lead and arsenic exposure is through oral exposure.

5.4.1 Lead

The likelihood of impact to human health from lead in soils was assessed using a number of different scenarios, where variability in concentration of lead in soil and bioavailability was considered.

It must be noted that bioavailability (Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007) is generally much lower than the more conservative estimate of potential uptake using bioaccessibility data, and thus the toxicity potential discussed is likely to be overestimated.

For the worst case scenario, based on the highest soil lead of 41,900 mg/kg coupled with the highest bioaccessibility of 25%, the dose, in terms of volume of soil required to be ingested to cause acute poisoning in an adult is 47.7 g and in a child is 9.5 g.

Chronic exposure to lead is based on the Provisional Tolerable Weekly Intake (PTWI) and the Acceptable Daily Intake (ADI) for whole of life. The health-based investigation threshold of the PTWI for exposure of lead, established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), is 25 μ g Pb/kg body weight (IPCS, 1995). For a 70 kg adult, ADI of lead is 0.25 mg (250 μ g). Similarly, for a child weighing 14 kg, the ADI is 0.05 mg (50 μ g).

Chronic Pb poisoning is not likely in adults. However, high lead in the soil (>2,400 mg/kg) could result in lead exposure exceeding the average daily intake in young children if the absolute bioavailability (ABA) of lead is greater than 10%. Similarly, a soil lead concentration >1200 mg/kg could result in lead exposure exceeding the allowable daily intake (ADI) in young children if the ABA of lead is greater than 20%. This conclusion is most relevant to residences where children spend a high frequency of their time. The health risk assessment calculations make an assumption that exposure to the contaminated site will be at least eight hours a day five days a week. Hence, the risk from the soil and sediments from the Leichhardt River as investigated is significantly less due to their classification as recreational areas.

5.4.2 Arsenic

As for lead, the likelihood of impact to human health from arsenic in soils was also assessed using a number of different scenarios, and considering a range of concentrations and bioavailability.

The highest concentration of arsenic found in the sampling program was 541 mg/kg. Assuming a theoretical ABA of 25% the amount of soil needed to acutely poison an adult person (70 kg body weight) is 0.518 kg to 1.555 kg; and 0.104 kg to 0.311 kg to acutely poison a child. The actual ABA of the site is likely to be

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

<25% (Bruce *et al.*, 2007; Diacomanolis *et al.*, 2007). The amount of soil with an arsenic concentration of 541 mg/kg that needs to be ingested by a child or adult to receive a toxic dose of arsenic is so great that this situation is unlikely to occur for a child or adult.

In the assessment on chronic exposure, it was demonstrated that a soil arsenic concentration of > 2000 mg/kg in conjunction with an ABA of 20% or higher and all sources of arsenic are considered, there is a potential risk for exceeding the ADI in children. When soil arsenic is > 10,000 mg/kg and the ABA is 2% or higher, there is a potential risk for exceeding the ADI in children. Table 15 shows that for soil arsenic of < 600 mg/kg there is no significant risk. The highest concentration of arsenic found throughout the sampling program was 541 mg/kg, which had a bioaccessibility of 1%. Thus, there was no significant risk associated with arsenic in the soil at the concentrations identified in this study.

5.5 Remediation of identified areas of contamination

Based on the analytical results presented in this study, remediation work was undertaken and has now been completed in those areas of the Leichhardt River that were shown to be impacted by historical mine sediments. The Leichhardt River Remediation Project was completed in May 2008 by Xstrata Mount Isa Mines. Contaminated material was removed between the Grace Street Bridge and downstream of the Velodrome. Included in the area of remediation were the majority of Sites at which soils where found to exceed NEPM HIL Level E guidelines, including L8, L10, L11 and L13.

A Summary Report on the completed Leichhardt River Remediation Project Works is provided in Appendix 5.

Further investigations, with the intent to undertake additional remediation activities as necessary, are being undertaken at Death Adder Gully, including Site L3 in Death Adder Gully and Site L12.

6.0 CONCLUSIONS

Initial comparisons of the soil concentrations against the NEPM HIL Level E criteria based on 100% bioavailability showed exceedances for arsenic, cadmium, cobalt, copper, lead and zinc at a number of sites. However, when the key contaminants of concern were adjusted for predicted bioavailability and compared once again with the NEPM HIL Level E criteria, only cadmium, copper, lead and zinc were in exceedance and at a reduced number of sites. Hence the area considered contaminated with respect to human health and requiring further investigation is significantly reduced by the application of bioaccessibility in a risk assessment process.

The investigation showed that sites at the swimming pool and the downstream sites in the Leichhardt River were not considered to be contaminated. However, the area of known contamination in the river between Grace Street Bridge and downstream of the Velodrome continued to show exceedances of the NEPM HIL Level E criteria once adjusted for bioavailability, for lead, copper, cadmium and zinc. Copper was also still in exceedance of the criteria at the Death Adder Gully sites.

The desktop human health risk assessment determined that contaminated soils, as sampled in this study, are unlikely to cause acute or sub chronic lead toxicity. It is also unlikely that chronic lead exposure would occur in adults. For arsenic in soil it is unlikely that it would cause acute toxicity, sub chronic, or chronic toxicity in humans because people are not likely to ingest sufficient amounts of soil under normal circumstances.

In a residential scenario, elevated lead concentrations in the soil of >2,400 mg/kg could result in chronic lead exposure in children if the bioavailability was greater than 10%. Equally, a soil lead concentration of >1200 mg/kg could result in chronic lead exposure in children if the bioavailability was greater than 20%. It must be noted that related studies have shown that lead bioavailability is generally much lower than bioaccessibility as used to predict bioavailability in this study. It should also be noted that in recreational areas such as the locations from the Leichhardt River investigated in this study, the risk is reduced even further due to the decreased frequency of exposure.

Results of the ecological risk assessment indicated that all sites exceeded one or both the ISQG–High and ISQG–Low trigger values based on total concentrations. A lesser number of sites exceeded the ISQG-Low trigger values once the 1M hydrochloric acid extract was used as an indication of bioavailability.

The subsequent assessment of the ecological health of the river using acute toxicity assessment on dry Leichhardt River sediment samples to two freshwater

crustacean species showed that only the zone of sediment adjacent to the Velodrome is toxic to the aquatic biota tested. Two sites (L9 and L12) adjacent to the Velodrome require further assessment to meet the ANZECC (2000) requirements for ecological risk assessment. All sites where sediment exceeded the ANZECC ISQG-Low trigger may require further ecological risk assessment by a more comprehensive suite of test organisms.

Testing of the potential acid-generation (and hence metal solubilisation) from waste rock samples used in the past in the structural armouring around the Velodrome in the Leichhardt River showed limited evidence that this was likely to be a significant source of further contamination.

Despite the fact that the risk to human health from historical mine sediments within the Leichhardt River was found to be low, the results presented in this study triggered the removal of historical mine sediments within the Leichhardt River. The Leichhardt River Remediation Project was completed by Xstrata Mount Isa Mines in May 2008.

Given the findings and observations from this initial study it is recommended that future investigations should include:

- (i) Verification sampling to confirm the success of the subsequent Leichhardt River Remediation Project in removing the contamination;
- (ii) An investigation into the cause of aquatic toxicity adjacent to the velodrome;
- (iii) Confirmation of sites requiring further detailed ecological risk assessment;
- (iv) Completion of a more detailed assessment of bioavailability of heavy metals, particularly lead, using animal uptake studies to give a more refined human health risk assessment and verify the predictive potential of the bioaccessibility technique for *in-vitro* bioavailability; and
- (v) Further development of knowledge on heavy metal pathways that may have the potential to impact on human health.

This study highlights the value of integrating human health and ecological health risk-based approaches to assess the significance of heavy metal and metalloid contamination.

7. PROFESSIONAL BACKGROUND

7.1 Centre for Mined Land Rehabilitation

Formally established in 1993, the Centre for Mined Land Rehabilitation (CMLR) at The University of Queensland (UQ) consists of a collaborative and multidisciplinary grouping of research, teaching and support staff and postgraduate students dedicated to delivering excellence in environmental research and education to the Queensland, national and international minerals industry and associated government sectors.

The Centre is widely recognised as the source of quality research and postgraduate students at the cutting edge of issues in mining environmental management and sustainability. It has built a reputation for the provision of the scientific research that is necessary to support and underpin the decisions that need to be made to minimise the environmental risks by the mining and processing of the full spectrum of commodities including coal, gold, bauxite, alumina, base metals, heavy mineral sands and oil, both in Australia and overseas.

The Centre is one of six UQ research centres that make up the Sustainable Minerals Institute (SMI – <u>www.smi.uq.edu.au</u>). The SMI was established in 2001 as a joint initiative of the Queensland Government, UQ and the minerals industry, to provide an over-arching framework for progressing minerals industry research and education, with the purpose of providing "knowledge-based solutions to meet the sustainability challenges in the global mining industry".

7.2 Experience of consultants

Associate Professor Barry Noller

Associate Professor Noller has a PhD (1978) in Environmental Chemistry from the University of Tasmania. He worked as a Research Fellow at the Australian National University (1978-1980), Senior Research Scientist at the Alligator Rivers Region Research Institute, Jabiru, Northern Territory (1980-1990) and then as Principal Environmental Chemist for the Department of Mines and Energy, Darwin Northern Territory (1990-1998). During this period Professor Noller was involved with the environmental management and regulation of all mines in the Northern Territory and was technical manager of the Northern Territory study on Bird Usage Patterns on Mining Tailings and their Management to Reduce Mortalities completed in 1998. He was also a co-author and reviewer of the Best Practice Environmental Management in Mining Handbook on Cyanide Management. From 1998-2006 Professor Noller was Deputy Director of the National Research Centre for Environmental Toxicology (EnTox) – The University of Queensland, Coopers Plains, Qld. EnTox has a strong involvement with the utilisation of the risk assessment process to deal with toxicological hazards, including in environmental systems. Since November 2006, Professor Noller has been appointed as Honorary Research Consultant and Principal Research Fellow at the Centre of Mined Land Rehabilitation (CMLR) a centre at The University of Queensland's St Lucia campus and a part of the Sustainable Minerals Institute.

Associate Professor Noller has been working and publishing in the field of environmental chemistry and industrial toxicology for the past 32 years and has presented >200 conference papers and published >130 papers. His professional activities undertaken at 4 different centres have covered processes and fates of trace substances in the environment, particularly in tropical environmental systems with special reference to risk management associated with their application and studies of the bioavailability of toxic elements in mine wastes, including waters. He has undertaken a number of consulting activities in Queensland, Tasmania, New South Wales and the Northern Territory and was appointed in 2007 as Lead Author of the Australian Government Leading Practice Sustainable Development Program for the Mining Industry Handbook on Cyanide Management.

Professor Jack Ng

Professor Ng is a certified toxicologist (DABT - Diplomate of the American Board of Toxicology) and is the Program Manager for Metals and Metalloids (M&M) Research at EnTox. His major research themes include chemical speciation of arsenic species in environmental and biological media, bioavailability in relationship to toxicities using various animal models, carcinogenicity and mechanistic studies of chronic arsenic toxicity in both humans and animals. Professor Ng and his team have recently demonstrated that a methylated metabolite (MMA^{III}) of arsenic is the proximal carcinogen in an *in-vivo* model. This is a landmark study in arsenic research in addition to his initial proof of the carcinogenic effect of inorganic arsenic in-vivo. One of his current interests is to identify early biomarkers for the diagnosis of arsenicosis in humans and animals using both chemical and molecular biological tools. Other research interests include toxicity of mixed metals, the transfer of heavy metals via the food chain from mine tailings and other mining wastes in addition to study on natural toxins in plants relevant to human health. Jack's projects represent a combination of independent effort as well as linkages through national and international collaboration.

Professor Ng is also the Program Leader for Risk Assessment in CRC-CARE (Co-operative Research Centre - Contamination Assessment and Remediation of the Environment). Professor Ng has over 270 publications including journal papers, book chapters and technical reports.

Dr Vitukawalu P. Matanitobua

Dr Matanitobua has studied environmental chemistry and toxicology at the National Research Centre for Environmental Toxicology (EnTox) at the University of Queensland, and received his PhD in 2007.
8. LIMITATIONS

CMLR has prepared this report for the use of Xstrata Mount Isa Mines Limited. It is prepared in accordance with the scope of work.

This report should be read in full. No responsibility is accepted for use of any part of this report in any other context or for any other purpose or by third parties. This report does not purport to give legal advice. Legal advice can only be given by qualified legal practitioners.

The methodology adopted and sources of information used by CMLR are outlined in this report. Our conclusions are based upon the analytical data presented in this report and our experience. Opinions and recommendations presented herein apply to the information available at the time of our investigation and cannot necessarily apply to matters of which CMLR is not aware and has not had the opportunity to evaluate.

9.0 REFERENCES

ADWG (2004) Australian Drinking Water Guidelines - National Water Quality Management Strategy. The National Health and Medical Research Council Canberra.

ANZECC (2000) Australian Water Quality Guidelines for Marine and Freshwaters

ANZFA (1994) Food Standard Code: Standard A12, Metals and Contaminants in Food. Retrieved in January 2001. Australia New Zealand Food Authority. <u>http://www.anzfa.gov.au</u>

ATSDR (1999) Toxicological Profile for Lead. U.S. Department of Health and Human Services, Public Health Services, Agency for Toxic Substances and Disease Registry.

ATSDR (2000) Toxicological Profile for Arsenic (update). U.S. Department of Health and Human Services, Public Health Services, Agency for Toxic Substances and Disease Registry.

ATSDR (2003) ATSDR Toxicological Profiles. CDRom, US Department of Health and Human Services.

Binder, S., Forney, D., Kaye, W. and Paschal, D. (1987). "Arsenic exposure in children living near a former copper smelter." *Bull Environ Contam Toxicol* **39**(1): 114-121.

Boutwell, R. K. (1963). "A carcinogenicity evaluation of potassium arsenite and arsanilic acid." *Agric Food and Chem* **11**: 381-385.

Bruce, S. L., Noller, B. N., Grigg, A.H., Mullen, B.F., Mulligan, D.R., Ritchie, P.J., Currey, N. and Ng, J.C. (2003). "A field study conducted at Kidston Gold Mine, to evaluate the impact of arsenic and zinc from mine tailing to grazing cattle." *Toxicology Letters* **137**(1-2): 23-34.

Bruce, S. L. (2004). Development of a risk assessment tool to reduce the impact of arsenic and lead toxicity from mine tailings. *PhD thesis: The University of Queensland.* **pp. 351**

Bruce, S. Noller, B., Matanitobua, V. and Ng, J. (2007) In Vitro Physiologicallybased Extraction test (PBET) and Bioaccessibility of Arsenic and lead from Various Mine Waste Materials. Journal of Toxicology and Environmental Health, Part A 70 1700-1711.

Calabrese, E. J., Barnes, R., Stanek III, E.J., Pastides, H., Gilbert, C.E., Veneman, P., Wang, X., Lasztity, A. and Kostecki, P.T. (1989). "How much soil

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

do young children ingest: An epidemiologic study." *Regulatory Toxicology and Pharmacology* **10**: 123-137.

Casteel, S. W., Cowart, R. P., Weis, C.P., Henningsen, G.M., Hoffman, E., Brattin, W.J., Guzman, R.E., Starost, M.F., Payne, J.T., Stockham, S.L., Becker, S.V., Drexler, J.W. AND Turk, J.R. (1997). "Bioavailability of lead to juvenile swine dosed with soil from the Smuggler Mountain NPL site of Aspen, Colorado." *Fundamental and Applied Toxicology* **36**(2): 177-187.

Cheng, Y. L., Preslan, J. E., Anderson, M.B. and George, W.J. (1991). "Solubility and bioavailability of lead following oral ingestion of vitrified slagged aggregate." *Journal of Hazardous Materials* **27**(2): 137-147.

Davis, A., Ruby, M. V. and Bergstrom, P.D. (1992). "Bioavailability of Arsenic and Lead in Soils from the Butte, Montana, Mining District." *Environmental Science & Technology* **26**(3): 461-468.

Diacomanolis, V., Ng, J.C. and Noller, B.N. (2007)."Development of mine site close-out criteria for arsenic and lead using a health risk approach" Proceedings of the Second International Seminar on Mine Closure 16-19 Santiago, Chile Eds. A. Fourie, M. Tibbert and J. Wiertz. pp 191-198.

Eaton, D. L., Gilbert S. G. (2008). Chapter 2: Principles of toxicology. <u>Casarett</u> and <u>Doull's Toxicology</u>, <u>The Basic Science of Poisons</u>. C. D. Klaassen (Ed.), McGraw Hill Medical, New York. Pp 11-43.

Ecowise (2005) Aquatic ecosystem monitoring program -2005 for Mount Isa Mines. Progress Report. Ecowise Environmental. Brisbane.

Ecowise (2006) Aquatic ecosystem monitoring program -2005 for Mount Isa Mines. Final Report. Report No. 2005/199. Ecowise Environmental. Brisbane.

enHealth (2004). "Environmental Health Risk Assessment. Guidelines for assessing human health risks from environmental hazards". Department of Health and Ageing and enHealth Council: Canberra, Australia.

Freeman, G. B., Johnson, J. D., Killinger, J.M., Liao, S.C., Davis, A.O., Ruby, M.V., Chaney, R.L., Lover, S.C. and Bergstrom, P.D. (1993). "Bioavailability of arsenic in soil Impacted by smelter activities following oral-administration in rabbits." *Fundamental and Applied Toxicology* **21**(1): 83-88.

Freeman, G. B., Johnson, J. D., Killinger, J.M., Liao, S.C., Feder, P.I., Davis, A.O., Ruby, M.V., Chaney, R.L., Lover, S.C. and Bergstrom, P.D. (1992). "Relative bioavailability of lead from mining waste soil in rats." *Fundamental and Applied Toxicology* **19**: 388-398.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

Freeman, G. B., Johnson, J. D., Liao, S.C., Feder, P.I., Davis, A.O., Ruby, M.V., Schoof, R.A., Chaney, R.L., and Bergstrom, P.D. (1994). "Absolute bioavailability of lead acetate and mining waste in rats." *Toxicology* **91**(2): 151-163.

Freeman, G. B., Schoof, R. A., Ruby, M.V., Davis, A.O., Dill, J.A., Liao, S.C., Lapin, C.A. and Bergstrom, P.D. (1995). "Bioavailability of arsenic in soil and house dust impacted by smelter activities following oral administration in cynomolgus monkeys." *Fundamental and Applied Toxicology* **28**(2): 215-222.

Groen, K., Vaessen, H., Kliest, J.J.G., de Boer, J.L.M., van Ooik, T., Timmerman, A. and Vlug, R.F. (1994). "Bioavailability of inorganic arsenic from bog orecontaining soil in the dog." *Environmental Health Perspectives* **102**(2): 182-184.

Hamel, S.C., Buckley, B., Lioy, P.J. (1998). "Bioaccessibility of metals in soils for different liquid to solid ratios in synthetic gastric fluid". *Environ. Sci. Tech*nol. 32(3): 358.

Hinwood, A., Jolly, D. J. and Sim, M.R. (1999). *International Journal of Environmental Health Research* **9**: 131-141.

Holmes, K. K., Shirai, J. H., Richter, K.Y. and Kissel, J.C. (1999). "Field measurement of dermal soil loadings in occupational and recreational activities." *Environmental research* **80**: 148-157.

IPCS (1994) Lead, Inorganic. Poisons Information Monographs (PIM 301), International Programme on Chemical Safety.

IPCS (1995) Environmental Health Criteria: Inorganic Lead. World Health Organisation, International Programme on Chemical Safety.

IPCS (2001) Environmental health criteria 224: arsenic and arsenic compounds. World Health Organisation, International Programme on Chemical Safety.

IRIS (1999) Arsenic: Integrated Risk Information System, U.S. Environmental Protection Agency. October 21, 1999. <u>http://epa.gov/iris/subst/index.html</u>.

ISO. (1983). Water Quality: Methods of Biological Sampling - Handnet Sampling of Aquatic Benthic Macroinvertebrates. Draft ISO International Standard.

Kimbrough, R. D., Falk, H. and Stehr, P. (1984). "Health Implication of 2,3,7,8-tetrachlorodibenzioxin (TCDD) contamination of residential soil." *Journal of Toxicology and Environmental Health* **14**: 47-93.

Kurokawa, Y., Takahashi, M., Maekawa, A. and Hayashi, Y. (1989). "Promoting effects of metal compounds on liver, stomach, kidney, pancreas, and sjin carcinogenesis." *J Am Coll Toxicol* **8**: 1235-1239.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

Mount Isa Mines (2003) Leichhardt River Stream Sediment Survey.

NEPC (1999) National Environmental Protection (Assessment of Site Contamination) Measures, National Environment Protection Council, Adelaide.

Ng, J. C., Johnson, D., Imray, P., Chiswell, B. and Moore, M.R. (1998). "Speciation of arsenic metabolites in the urine of occupational workers and experimental rats using an optimised hydride cold- trapping method." *Analyst* **123**(5): 929-933.

Ng, J. C., Kratzmann, S. M., Qi, L., Crawley, H., Chiswell, B. and Moore, M.R. (1998). "Speciation and absolute bioavailability: risk assessment of arsenic-contaminated sites in a residential suburb in Canberra." *Analyst* **123**(5): 889-892.

Ng J.C. (1999) Speciation, bioavailability and toxicity of arsenic in the environment. PhD thesis, the University of Queensland. 324pp.

Ng, J. C., Noller, B. N. Bruce, S. and Moore. M.R. (2003). Bioavailability of metals and arsenic contaminated sites from cattle dips, mined land and naturally occurring mineralisation origins. Fifth National Workshop on the Assessment of Site Contamination. Eds. A. Langley, M. Gilbey and B. Kennedy.. Adelaide, EHPC/enHealth. Adelaide. pp 163-181.

NHMRC (1990) Ambient Air Quality Goals Recommended by NHMRC and Interim National Air Quality Goals Recommended by NHMRC. National Health and Medical Research Council.

NRC (1999) Arsenic in drinking water. National Academy Press,

NRC (2003) Bioavailability of Contaminants in Soil and Sediments. National Research Council of the National Academies Press: Washington, D.C.

NR&M (Queensland Department of Natural Resources & Mines) (2001). Queensland AusRivAS sampling and processing manual, August 2001. NR&M Technical Centre, Rocklea, Queensland.

NSW EPA (2003) Pathways of exposure to lead. New South Wales Environmental Protection Agency. <u>http://www.epa.nsw.gov.au/leadsafe/04337636-7b21-402f-bf4f-afc6e5eba6e,ced3b86</u>

Oomen, A. G., Hack, A., Cornelis, C., Schoeters, G., Verstraete, W., Van De Wiele, T., Wragg, J., Rompelberg, C. J. M., Sips, A. J. A. M. and Van Wijnen, J. H. (2002). Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environmental Science & Technology* **36**: 3326-3334.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

Paustenbach, D. J. (1989) A comprehensive methodology for assessing the risks to humans and wildlife posed by contaminated soils: A case study involving dioxin. In: The risk assessment for environmental hazards: A Textbook of case studies. D. Paustenbach, J, (Ed).

Queensland Health (2008) Mt Isa Community Lead Screening Report (2006/7) <u>http://www.health.qld.gov.au/ph/documents/tphn/mtisa_leadrpt.asp</u> Queensland Health, Queensland Government Brisbane Qld.

Roberts, S. M., Weimar, W. R., Vinson, J.R.T., Munson, J.W. and Bergeron, R.J. (2002). "Measurement of arsenic bioavailability in soil using a primate model." *Toxicological Sciences* **67**(2): 303-310.

Ruby, M. V., Davis, A., Schoof, R., Eberle, S. and Sellstone, C.M. (1996). "Estimation of lead and arsenic bioavailability using a physiologically based extraction test." *Environmental Science and Technology* **30**(2): 422-430.

Ruby, M. V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D.E., Casteel, W., Berti, W., Carpenter, M., Edwards, D., Cragin, D. and Chappell, W. (1999). "Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment." *Environmental Science & Technology* **33**(21): 3697-3705.

Rodriguez, R. R., Basta, N. T., Casteel, S. W. and Pace, L. W. (1999). An in vitro gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environmental Science & Technology* **33**(4): 642-649.

Sadler, R., Olszowy, H., Shaw, G. and Neville, G. (1990). Report on Contaminated Sites at Mt Isa. Queensland Government Chemical Laboratory and Division of Environmental and Occupational Health. GCL Report Series No. 5, Sept 1990.

Shraim, A., Cui, X., Li, S., Ng, J.C, Wang, J., Jin, Y., Liu, Y., Guo, L., Li, D., Wang, S., Zhang, R. and Hirano, S. (2003). "Arsenic speciation in the urine and hair of individuals exposed to airborne arsenic through coal-burning in Guizhou, PR China." *Toxicology Letters* **137**(1-2): 35-48.

Standards Australia (2005) Australian Standard AS 4482.1: Guide to the sampling and investigation of potentially contaminated soil - Non-volatile and semi-volatile compounds. Standards Australia: 1 The Crescent, Homebush NSW 2140 Australia).

Sun, C. C., Wong, R. T., Hwang, Y.H., Chao, K.Y., Jee, S.H., and Wang, J.D. (2002). "Percutaneous absorption of inorganic lead compounds." *AIHA Journal* **63**: 641-646.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

Surtikanti, H.K. and Hyne, R.V. (2000) Sediment toxicity testing using the amphipod *Corophium sp*: Standardisation of the test conditions for an acute survival test and a sub-chronic growth test in freshwater. Australasian Journal of Ecotoxicology 6: 11-20.

Taylor, E. R. (1991). How much soil do children eat? In: The Health Risk Assessment and Management of Contaminated Sites. Proceedings of a National Workshop on the Health Risk Assessment and Management of Contaminated Sites. O. El Saadi and A. Langley (eds). South Australian Health Commission.

Tseng, W. P., Chu, H. M., How, S.W., Fong, J.M., Lin, C.S. and Yeh, S. (1968). "Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan." *J Natl Cancer Inst* **40**: 453-463.

U.S. EPA (1996) Bioavailability of arsenic and lead in environmental substrates. 1. Results of an oral dosing study of immature swine. Superfund/Office of Environmental Assessment, EPA 910/R-96-002. www.epa.gov/r10earth/offices/oea/risk/bioavail.pdf

U.S. EPA (1998) Guidelines for ecological risk assessment; U.S. Environmental Protection Agency: Washington, DC, pp 188.

U.S.EPA (2001) National primary drinking water regulations; arsenic and clarifications to compliance and new source contaminants monitoring; final rule. J. Federal Register, 2001. USEPA

USEPA (2007) "Estimation of relative bioavailability of lead in soil and soil-like materials using in vivi and in vitro methods". Report No. OSWER 9285.7-77 May 2007. U.S. Environmental Protection Agency, Washington, DC 20460.

Vallee, B. L., Ulmer, D. D. and Wacker, W.E.C.(1960). "Arsenic toxicology and biochemistry." *Arch Ind Health* **21**: 132-151.

Wahlberg, J. E. and A. Boman (1896). "Contact sensitivity to arsenic compounds: clinical and experimental studies." *Derm Beruf Umwelt* **34**: 10-12.

Wester, R. C., Maibach, H. I., Sedik, L., Melendres, J. and Wade, M. (1993). "In vivo and in vitro percutaneous absorption and skin decontamination of arsenic from water and soil." *Fundam Appl Toxicol* **23**(3): 336-340.

WHO (1989) Evaluation of certain food additives and contaminants. Thirty-third report of the Joint FAO/WHO Expert Committee on Food Additive. World Health Organisation Technical Report Series 776. WHO.

Worksafe Australia (1995) Exposure Standards for Atmospheric Contaminants in the Occupational Environment. Worksafe Australia.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

10. APPENDICES

Appendix 1 Location of sampling sites

				Sample	Analysis					
		Coordinate	es	Soil (<2	mm)	Sedime	nt (<63um)		Acid potential material	
Sampling Site Details	Site	Easting	Northing	Total Digest	PBET	Total Digest	0.1 M HCI (ANZECC Sediment)	PBET		Comments
LR - Upstream (background)	L1	343416	7700904	1	1		1	1		5 sampling points for both sediment and soil composite samples (West of Leichhardt River)
Death Adder Gully (West)	L2	342156	7706812	1	1					6 sampling points for composite sample
Death Adder Gully (East)	L3	342468	7706754	1	1					5 sampling points for composite sample
Skate Park (grassed area at depth) Swimming Pool Area	L4	342336	7707040	1	1					Composite sample (5 sample points over dirt jumping area, 6 sample points for grassed area)
Skate Park (ungrassed parking area) Swimming Pool Area	L5	342275	7706970	1	1					10 sampling points for composite sample
Kruttschnitt Oval adjacent to Swimming Pool Area	L6	342416	7706878	1	1					7 sampling points for composite sample

LR - Between Isa Street Crossing and Grace Street Bridge	L7	342523	7707217			1	1		6 sampling points for composite sample
LR - Historical Tailings (between Grace street bridge and Velodrome)	L8	342452	7707513	1	1				10 sampling points for composite sample
LR - Downstream/East of Velodrome	L9	342676	7708051			1	1		10 sampling points for composite sample
LR - Velodrome East (Acid Gen Material)	L10	342539	7707664	1	1			1	10 sample points for soil sample, 20 sample points for Acid Gen. material
LR - Velodrome West (Acid Gen Material)	L11	342417	7707666	1	1			1	10 sample points for soil sample, 20 sample points for Acid Gen. material
LR - Pipe exit	L12	342357	7707643			1	1		12 sampling points for composite sample
LR - Historical Tailings West embankment	L13	342386	7707891	1	1				11 sampling points for composite sample
LR - Historical Tailings deposition (mid channel)	L14	342555	7708232	1	1				10 sampling points for composite sample
LR - Fluvial downstream (Moondarra)	L15	343454	7713760	1	1	1	1		

LR - Downstream of Lake Moondarra (Leichhardt River)	L16	353578	7723640	1	1	1	1	1		
--	-----	--------	---------	---	---	---	---	---	--	--

Appendix 2 Macroinvertebrate data summaries (Ecowise 2005, 2006)

Macroinvertebrate Results – Raw Data (March 2005)

5121914		Site 1 - Browns	Site 2 - Leichhardt	Site 3 - Isa St	Site 4 - Davis Rd	Site 5 - Moondarra	Site 6 - Glenroy
Ecowise Environmental	Site	Waterhole	U/S	Bridge	Xing	Rd Xing	Dam
Linnonnentor	Habitat	Edge	Edge	Edge	Edge	Edge	Edge
Order	Family						
Acarina		20	37	29	21	4	25
Bivalvia	Hyriidae		2		1		1
Coleoptera	Dytiscidae	1	1	6			8
	Hydraenidae		1			2	4
	Hydrophilidae		6		5		
Crustacea	Cladocera			1	3		2
	Copepoda	2		3	6		1
	Ostracoda	6		1		1	1
Decapoda	Palaemonidae		1			3	
	Parastacidae				1	2	
Diptera	Ceratopogonidae	1	9		2	5	5
	Chaoboridae		1				
	Culicidae			1			
	Ephydridae				1		
	s-f Chironominae	13	13	15	17	23	28
	s-f Orthocladiinae			2			
	s-f Tanypodinae	26	12	10	22	8	8
	Tabanidae	1					1
Ephemeroptera	Baetidae	1	5	12	11		8
	Caenidae	16	21	5	2	2	13
	Leptophlebiidae						1
Gastropoda	Ancylidae			1			
	Lymnaeidae					1	
	Planorbidae		2		1		
Hemiptera	Corixidae	7	6	8	18	1	1
	Gerridae		12	2	1	1	
	Mesoveliidae						2
	Nepidae			1		2	
	Notonectidae		3	1			6
	Pleidae		2	11	10	13	8
	Veliidae						2
Odonata	Coenagrionidae			16	14	2	2
	Gomphidae	8	2	1	3		
	H/U/L complex		1	1			
	Hemicorduliidae					2	1
	Isostictidae	8	1				1
	Lestidae			2			
	Libellulidae	1			6		
	Lindeniidae		2	1	2	1	1
	Zygoptera			5	5	1	
Oligochaeta					1	8	
Trichoptera	Ecnomidae	3	6	1	3	2	10
	Hydroptilidae				1		[
	Leptoceridae		5	2		1	4
	Taxa Richness	15	23	25	24	21	25

Phylum	sub phylum	Class	Order	si Family fa	ıb mily	Site 3 - Isa St Bridge	Site 4 - Davis Rd Crossing	Site 5 - Moondarra Rd Crossing	Site 6 - Glenroy Dam
Annelida	.	Oligochaeta				3	3	1	
].								
Mollusca	.	Bivalvia		Corbiculidae				1	
	Į	Gastropoda		Lymnaeidae			6		
	l			Physidae			5		
	Į			Planorbidae		2	7		
]			Thiaridae				4	
Arthropo	da	Arachnida	Acarina			6	5	1	. 11
	Crustacea	Cladocera				10		5	
		Copepoda				6	2	1	1
		Ostracoda				2	2	2	
			Decapoda	Palaemonidae		2		1	4
	Hexipoda	Insecta	Coleoptera	Dytiscidae		4		6	17
				Hydraenidae		3			1
				Hydrochidae		8	1		8
				Hydrophilidae		2	8	13	10
	[Diptera	Ceratopogonidae		9		1	6
].	L		Culicidae		7	3	3	10
				Chironomidae					
				Chirono	minae	31	15	13	14
				Tanypo	dinae	5	10	19	7
]			Stratiomyidae		11	1	2	
			Ephemeroptera	Baetidae		3	8	13	10
				Caenidae				6	. 11
			Hemiptera	Belostomatidae					1

Macroinvertebrate Results – Raw Data (September 2005)

Phylum	Class	sub Order order	Family	Site 3 - Isa St Bridge	Site 4 - Davis Rd Crossing	Site 5 - Moondarra Rd Crossing	Site 6 - Glenroy Dam
		Hemiptera	Corixidae	13	8	12	10
			Gerridae	[5	1	
			Hebridae	1	1		1
			Nepidae	1	1		1
			Notonectidae		1	3	
			Pleidae	11	3	4	10
			Veliidae		3	1	4
		Lepidoptera	Pyralidae			3	
		Odonata					
		Zygoptera	Coenagrionidae	15	13	14	2
		Epiproctophor	Aeshnidae	3	6	1	
			Gomphidae				4
			Libellulidae	. 9	9	7	2
			Lindeniidae		1		1
			unknown	1		2	
		Trichoptera	Ecnomidae	2	2	1	5
			Hydroptilidae	1			
			Leptoceridae	12	14	15	10

Macroinvertebrate Results – Raw Data (September 2005) Cont.

Appendix 3 Acid Potential Results



ALS Environmental

		CERT	IFICATE OF ANALYSIS		
Client	: THE UNIVERSITY OF QUEENSLAND	Laboratory	: Environmental Division Brisbane	Page	∵ 1 of 4
Contact	MR BARRY NOLLER	Contact	: Tim Kilmister	Work Order	EB0705949
Address	: CENTRE FOR MINED LAND REHABILITATION, THE UNIVERSITY OF QUEENSLAND ST LUCIA QLD AUSTRALIA 4072	Address	32 Shand Street Stafford QLD Australia 4053		220,00010
E-mail	: b.noller@uq.edu.au	E-mail	Services.Brisbane@alsenviro.com		
Telephone	33653457	Telephone	: 61-7-3243 7222		
Facsimile	33653452	Facsimile	÷ 61-7-3243 7259		
Project	: - Not provided -	Quote number	:	Date received	: 31 May 2007
Order number	: - Not provided -			Date issued	: 12 Jun 2007
C-O-C number	: - Not provided -			No. of samples	- Received : 2
Site	: - Not provided -				Analysed : 2

ALSE - Excellence in Analytical Testing

			, many acta recounty				
	NATA Accredited Laboratory 825 This document has been electronically signed by those names that appear on this report and are the authorised signatories. Electronic signing has been carried out in compliance with procedures specified in 21 CFR Part 11.						
NATA	This document is issued in	Signatory	Position	Department			
NAIA	accordance with NATA's accreditation requirements	Kim McCabe	Senior Inorganic Chemist	Inorganics - NATA 825 (818 - Brisbane)			
		Stephen Hislop	Senior Inorganic Chemist	Inorganics - NATA 825 (818 - Brisbane)			
\mathbf{v}		Stephen Hislop	Senior Inorganic Chemist	Stafford Minerals - NATA 825 (818 -			
WORLD RECOGNISED	Accredited for compliance with ISO/IEC 17025			Brisbane)			

 Page Number
 : 2 of 4

 Client
 : THE UNIVERSITY OF QUEENSLAND

 Work Order
 : EB0705949

Comments

This report for the ALSE reference EB0705949 supersedes any previous reports with this reference. Results apply to the samples as submitted. All pages of this report have been checked and approved for release.

This report contains the following information:

- Analytical Results for Samples Submitted
- Surrogate Recovery Data

The analytical procedures used by ALS Environmental have been developed from established internationally-recognized procedures such as those published by the US EPA, APHA, AS and NEPM. In house developed procedures are employed in the absence of documented standards or by client request. The following report provides brief descriptions of the analytical procedures employed for results reported herein. Reference methods from which ALSE methods are based are provided in parenthesis.

When moisture determination has been performed, results are reported on a dry weight basis. When a reported 'less than' result is higher than the LOR, this may be due to primary sample extracts/digestion dilution and/or insuffient sample amount for analysis. Surrogate Recovery Limits are static and based on USEPA SW846 or ALS-QWI/EN38 (in the absence of specified USEPA limits). Where LOR of reported result differ from standard LOR, this may be due to high moisture, reduced sample amount or matrix interference. When date(s) and/or time(s) are shown bracketed, these have been assumed by the laboratory for process purposes. Abbreviations: CAS number = Chemical Abstract Services number, LOR = Limit of Reporting. * Indicates failed Surrogate Recoveries.





Page Number	: 3 of 4
Client	THE UNIVERSITY OF QUEENSLAND
Work Order	: EB0705949

Analytical Results	Sample Mat	Client Sample ID : Ix Type / Description : Sample Date / Time : aboratory Sample ID :	L10 SOIL (29 May 2007) (15:00)	L11 SOIL (29 May 2007) (15:00)		
Analyte	CAS number	OR Units	EB0705949-001	EB0705949-002		
EA009: Nett Acid Production Potentia	I					
Net Acid Production Potential	0	.5 kg H2SO4/t	122	-15.0		
EA011: Net Acid Generation						
pH (OX)	0	.1 pH Unit	7.8	7.9		
NAG (pH 4.5)	0	.1 kg H2SO4/t	<0.1	<0.1		
NAG (pH 7.0)	0	.1 kg H2SO4/t	<0.1	<0.1		
EA013: Acid Neutralising Capacity						
ANC as H2SO4	0	.5 kg H2SO4	57.9	99.2		
		equ				
Fizz Rating		I Fizz Unit	2	2		
EA031: pH (saturated paste)						
pH (Saturated Paste)	0	.1 pH Unit	5.9	6.9		
EA032: Electrical Conductivity (satur	ated paste)					
Electrical Conductivity (Saturated Paste)		I μS/cm	3450	3510		
ED042T: Total Sulphur by LECO						
Sulphur - Total as S (LECO)	0.	D1 %	5.89	2.75		

A Campbell Brothers Linkted Company

 Page Number
 : 4 of 4

 Client
 : THE UNIVERSITY OF QUEENSLAND

 Work Order
 : EB0705949

Surrogate Control Limits



No surrogates present on this report.

Report version : COANA 3.02

A Campbell Brothers Linkted Company

Appendix 4 Acute Toxicity Assessment of Dry Sediment Samples to Two Crustacean Species and Aquatic toxicity heavy metals in elutriate results Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



Acute Toxicity Assessment of Dry Sediment Samples to Two Crustacean Species

Centre for Mined Land Rehabilitation, University of Queensland

Test Report

November 2007



Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



Acute Toxicity Assessment of Dry Sediment Samples to Two Crustacean Species

Centre for Mined Land Rehabilitation, University of Queensland

Test Report

November 2007



Centre for Mined Land Rehabilitation, The University of Queensland: June 2009





Toxicity Test Report: TR0326/1

(page 1 of 2)

Client: Attention: Contract #: 2366 2367 2368 2369 2370 2371	Centre for Mined La University of Queen: Brisbane QLD 4072 Dr Barry Noller n/a Sample Name: L1 L7 L9 L12 L12 L15 L16	nd Rehabilitation Iland	ESA Job #: Date Sampled: Date Received: Sampled By: Quote #: Sample Descriptio Dry sediment Dry sediment Dry sediment Dry sediment Dry sediment Dry sediment	PR0326 4 September 200 28 September 20 Client PL0326_q01 n:	7 07	
Test Performe	d.	18-br acute (survival)	toxicity test using the	freshwater cladocerar		
Test Performed: 48-hr acute (surviva) toxicity test using the freshwater cladoceran Ceriodaphnia cf dubia Test Protocol: ESA SOP 101, based on USEPA (1993) Deviations from Protocol: Tests were conducted on elutriate prepared from the dry sediment is mixed with dilution water at a ration of 1:4, stirred and allowed to settle for 2h prior to preparation of dilution series and seeding with test organisms. Source of Test Organisms: ESA Laboratory culture 24 October 2007 at 1700h						
Sample 2366 Concentrati (%)	i: <i>L1</i> on % Survival (at 48 hr)	Sample 2367: L Concentration (%)	.7 % Survival (at 48 hr)	Sample 2368: L9 Concentration (%)	% Survival (at 48 hr)	
0 (control)	100 ± 0.0	0 (control)	100 ± 0.0	0 (control)	100 ± 0.0	
6.25	100 ± 0.0	6.25	100 ± 0.0	6.25	0.0 ± 0.0	
12.5 25 50 100	$\begin{array}{c} 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \end{array}$	12.5 25 50 100	$\begin{array}{c} 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \end{array}$	12.5 25 50 100	$\begin{array}{c} 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \end{array}$	
48 hr EC50 = NOEC = 100 LOEC = >10	= >100% % 0%	48 hr EC50 = > NOEC = 100% LOEC = >100%	100%	48 hr EC50 = <6.2 NOEC = <6.25% LOEC = 6.25%	5%	



Centre for Mined Land Rehabilitation, The University of Queensland: June 2009





Toxicity Test Report: TR0326/1

(page 2 of 2)

Sample 2369: L12 Concentration (%)	% Survival (at 48 hr)	Sample 2370: L18 Concentration (%)	5 % Survival (at 48 hr)	Sample 2371: L10 Concentration (%)	ි % Survival (at 48 hr)
0 (control)	100 ± 0.0	0 (control)	100 ± 0.0	0 (control)	100 ± 0.0
6.25	0.0 ± 0.0	6.25	100 ± 0.0	6.25	100 ± 0.0
12.5 25 50 100	$\begin{array}{c} 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.0 \pm 0.0 \end{array}$	12.5 25 50 100	$\begin{array}{c} 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \end{array}$	12.5 25 50 100	$\begin{array}{c} 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \\ 100 \pm 0.0 \end{array}$
48 hr EC50 = <6.2 NOEC = <6.25% LOEC = 6.25%	25%	48 hr EC50 = >10 NOEC = 100% LOEC = >100%	0%	48 hr EC50 = >10 NOEC = 100% LOEC = >100%	00%

QA/QC Parameter	Criterion	This Test	Criterion met?
Control minimum % survival	>70 %	100%	Yes
Test Temperature limits	25.0 ± 1 °C	25.0°C	Yes
Reference Toxicant within cusum chart limits	137.0-252.7mg/L	212.1mg/L	Yes



port Authorised by: Dr Rick Krassoi, Director on 29 November 2007

Results are based on the samples in the condition as received by ESA

NATA Accredited Laboratory Number: 14709

The tests, calibrations or methods covered by this document have been performed in accordance with NATA requirements which include the requirements of ISO/IEC 17025 and are traceable to Australian national standards of measurement. This document shall not be reproduced except in full.





Toxicity Test Report: TR0326/2

(page 1 of 1)

Client: Attention: Contract #:	Centre for Mined Land Rehabilit University of Queensland Brisbane QLD 4072 Dr Barry Noller n/a	ation ESA Job #: Date Sampled: Date Received: Sampled By: Quote #:	PR0326 4 September 2007 28 September 2007 Client PL0326_q01
Lab ID No.:	Sample Name:	Sample Description	n:
2366	L1	Dry sediment	
2367	L7	Dry sediment	
2368	L9	Dry sediment	
2369	L12	Dry sediment	
2370	L15	Dry sediment	
2371	L16	Dry sediment	
Test Performe	ed: 10-day who amphipod C	e sediment survival toxicity test corophium spp.	using the estuarine
Test Protocol	: ESA SOP 1	09, based on USEPA (1996)	

restrictoron.	ECA COT 100, Dased on COELA (1550)
Deviations from Protocol:	Nil
Source of Test Organisms:	Field collected from Wisemans Ferry on 22 October 2007
Test Initiated:	30 October 2007 at 1300h

Sample 2366-237 Sample	1 % Survival (at 10 Days)	Vacant	Vacant
Control	92.5 ± 5.0		
L1	75.0 ± 12.9		
L7 L9	90.0 ± 8.2 0.0 ± 0.0		
L12	0.0 ± 0.0		
L15	82.5 ± 15.0		
L16	90.0 ± 0.0		

The concentration of total ammonia and sulphide in the overlying water in all sample treatmentents at Day 0 was <2.0 and <0.10 mg/L, respectively.

QA/QC Parameter	Criterion	This Test	Criterion met?
Control minimum % survival	>70 %	92.5%	Yes
Test Temperature limits	20.0 ± 1 °C	19.5-20.5°C	Yes
Reference Toxicant within cusum chart limits	125-3189µg/L	488µg/L	Yes

Test Report Authorised by:

Dr Rick Krassoi, Director on 29 November 2007

Results are based on the samples in the condition as received by ESA This document shall not be reproduced except in full.

For Vami



Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



Statistical Analyses of Toxicity Test Data

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009

			Cerio	daphnia Surv	vival and Reproduction Test-48 Hr Survival
Start Date:	10/24/2007	17:00	Test ID:	PR0326/01	Sample ID: L1
End Date:	10/26/2007	17:00	Lab ID:	2366	Sample Type: Sediment Elutriate
Sample Date:			Protocol:	ESASOP101	Test Species: CD-Ceriodaphnia dubia
Comments:					
Conc-%	1	2	3	4	
DMW Control	1.0000	1.0000	1.0000	1.0000	
6.25	1.0000	1.0000	1.0000	1.0000	
12.5	1.0000	1.0000	1.0000	1.0000	
25	1.0000	1.0000	1.0000	1.0000	
50	1.0000	1.0000	1.0000	1.0000	
100	1.0000	1.0000	1.0000	1.0000	

		_	T	ransform:	Arcsin Sq	uare Root		Rank	1-Tailed
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	Ν	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
6.25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
12.5	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
50	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
100	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00

	Auxiliary Tests					Statistic	Critical	SKew
	Shapiro-Wilk's Test indicates normal	distribution	(p > 0.01)			1	0.884	
	Equality of variance cannot be confirm	med						
	Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	ΤU			
ľ	Steel's Many-One Rank Test	100	>100		1			



Dose-Response Plot

Page 1

ToxCalc v5.0.23

		Ceri	odaphnia Su	rvival and	Reprod	uction Test-4	48 Hr Su	rvival	
Start Date:	10/24/2007 17:00	Test ID:	PR0326/01			Sample ID:		L1	
End Date:	10/26/2007 17:00	Lab ID:	2366			Sample Typ	e:	Sediment	Elutriate
Sample Date:		Protocol:	ESASOP101	1		Test Specie	S:	CD-Cerio	daphnia dubia
Comments:									
				Au	xiliary Da	ata Summary	/		_
Conc-%	Parameter		Mean	Min	Мах	SD	CV%	N	
DMW Control	% Survival		100.00	100.00	100.00	0.00	0.00	4	
6.25			100.00	100.00	100.00	0.00	0.00	4	
12.5			100.00	100.00	100.00	0.00	0.00	4	
25			100.00	100.00	100.00	0.00	0.00	4	
50			100.00	100.00	100.00	0.00	0.00	4	
100			100.00	100.00	100.00	0.00	0.00	4	_
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50			25.00	25.00	25.00	0.00	0.00	1	
100			25.00	25.00	25.00	0.00	0.00	1	_
DMW Control	рН		8.10	8.10	8.10	0.00	0.00	1	
6.25			8.10	8.10	8.10	0.00	0.00	1	
12.5			8.20	8.20	8.20	0.00	0.00	1	
25			8.10	8.10	8.10	0.00	0.00	1	
50			8.10	8.10	8.10	0.00	0.00	1	
100			8.00	8.00	8.00	0.00	0.00	1	_
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	
6.25			102.30	102.30	102.30	0.00	0.00	1	
12.5			102.70	102.70	102.70	0.00	0.00	1	
25			101.40	101.40	101.40	0.00	0.00	1	
50	0		101.20	101.20	101.20	0.00	0.00	1	
10	U Conductivity vO	lana	98.70	98.70	98.70	0.00	0.00	1	-
DIMINI Contro	Gonauctivity uS	/cm	171.10	171.10	171.10	0.00	0.00	1	
6.2	5		172.10	172.10	172.10	0.00	0.00	1	
12.	5		172.10	172.10	172.10	0.00	0.00	1	
2	0		172.00	172.00	172.80	0.00	0.00	4	
5	0		174.00	174.00	176.70	0.00	0.00	1	
10	U		176.70	176.70	176.70	0.00	0.00	1	_

ToxCalc v5.0.23

			Cerie	odaphnia Surv	vival and Reproduction Test-48 Hr Survival	
Start Date:	10/24/2007	17:00	Test ID:	PR0326/02	Sample ID: L7	
End Date:	10/26/2007	17:00	Lab ID:	2367	Sample Type: Sediment Elutriate	
Sample Date:			Protocol:	ESASOP101	Test Species: CD-Ceriodaphnia dubia	3
Comments:						
Conc-%	1	2	3	4		
DMW Control	1.0000	1.0000	1.0000	1.0000		
6.25	1.0000	1.0000	1.0000	1.0000		
12.5	1.0000	1.0000	1.0000	1.0000		
25	1.0000	1.0000	1.0000	1.0000		
50	1.0000	1.0000	1.0000	1.0000		
100	1.0000	1.0000	1.0000	1.0000		

		_	Transform: Arcsin Square Root						1-Tailed
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	N	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
6.25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
12.5	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
50	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
100	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00

					A			Bank	4 Tailed
		_	TI	ransform:	Arcsin Sq	uare Root		Rank	1-Tailed
Conc-%	Mean	N-Mean	Mean	Min	Мах	CV%	Ν	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
6.25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
12.5	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
50	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
100	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00

Auxiliary Tests					Statistic	Critical	Skew
Shapiro-Wilk's Test indicates norma	l distribution	(p > 0.01)			1	0.884	
Equality of variance cannot be confi	med						
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	τu			
Steel's Many-One Rank Test	100	>100		1			

Dose-Response Plot



ToxCalc v5.0.23

		Ceri	odaphnia Su	rvival and	Reprod	uction Test-4	18 Hr Su	rvival	
Start Date:	10/24/2007 17:00	Test ID:	PR0326/02			Sample ID:		L7	
End Date:	10/26/2007 17:00	Lab ID:	2367			Sample Typ	e:	Sediment I	Elutriate
Sample Date:		Protocol:	ESASOP101			Test Species	S:	CD-Ceriod	aphnia dubia
Comments:									
				Au	xiliary Da	ata Summary	1		
Conc-%	Parameter		Mean	Min	Max	SD	CV%	N	
DMW Control	% Survival		100.00	100.00	100.00	0.00	0.00	4	
6.25			100.00	100.00	100.00	0.00	0.00	4	
12.5			100.00	100.00	100.00	0.00	0.00	4	
25			100.00	100.00	100.00	0.00	0.00	4	
50			100.00	100.00	100.00	0.00	0.00	4	
100			100.00	100.00	100.00	0.00	0.00	4	
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50			25.00	25.00	25.00	0.00	0.00	1	
100			25.00	25.00	25.00	0.00	0.00	1	
DMW Control	pН		8.10	8.10	8.10	0.00	0.00	1	
6.25			8.10	8.10	8.10	0.00	0.00	1	
12.5			8.10	8.10	8.10	0.00	0.00	1	
25			8.10	8.10	8.10	0.00	0.00	1	
50			8.10	8.10	8.10	0.00	0.00	1	
100			8.10	8.10	8.10	0.00	0.00	1	
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	
6.25			103.10	103.10	103.10	0.00	0.00	1	
12.5			102.00	102.00	102.00	0.00	0.00	1	
25			101.80	101.80	101.80	0.00	0.00	1	
50			101.40	101.40	101.40	0.00	0.00	1	
100			99.60	99.60	99.60	0.00	0.00	1	
DMW Control	Conductivity US/	cm	171.10	171.10	171.10	0.00	0.00	1	
6.25	contracting don		172.80	172.80	172.80	0.00	0.00	1	
12.5			174.30	174.30	174.30	0.00	0.00	1	
25			177.00	177.00	177.00	0.00	0.00	1	
50			182.60	182.60	182.60	0.00	0.00	1	
100			102.00	102.00	102.00	0.00	0.00		

ToxCalc v5.0.23

			Cerio	odaphnia Surv	vival and Reproduction Test-48 Hr Survival
Start Date:	10/24/2007	17:00	Test ID:	PR0326/03	Sample ID: L9
End Date:	10/26/2007	17:00	Lab ID:	2368	Sample Type: Sediment Elutriate
Sample Date:			Protocol:	ESASOP101	Test Species: CD-Ceriodaphnia dubia
Comments:					
Conc-%	1	2	3	4	
DMW Control	1.0000	1.0000	1.0000	1.0000	
6.25	0.0000	0.0000	0.0000	0.0000	
12.5	0.0000	0.0000	0.0000	0.0000	
25	0.0000	0.0000	0.0000	0.0000	
50	0.0000	0.0000	0.0000	0.0000	
100	0.0000	0.0000	0.0000	0.0000	

		_	T	ransform:	Arcsin Sq	uare Root		Rank	1-Tailed
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	Ν	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
*6.25	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00
*12.5	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00
*25	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00
*50	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00
*100	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00

Auxiliary Tests					Statistic	Critical	Skew
Shapiro-Wilk's Test indicates norma	al distribution	(p > 0.01)			1	0.884	
Equality of variance cannot be cont	firmed						
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	ΤU			
Steel's Many-One Rank Test	<6.25	6 25					



ToxCalc v5.0.23

Start Date:	10/24/2007 17:00	Teet ID:	DD0326/02			Sample ID:		10	
Sidii Dale.	10/24/2007 17:00	Test ID.	PR0326/03			Sample ID.		Codimont	Elutrioto
End Date:	10/26/2007 17:00	Lab ID.	2368			Sample Typ	be.	Sediment	Elumate
Sample Date.		Protocol.	ESASOPTU	I		Test Specie	es.	CD-Cerio	aphnia dubia
comments.									
Cono N	Deveneter		Maan	AL	IXIIIary Da	ata Summar	y 0\/%	N	-
DMW/ Control			100.00	MIN 100.00	100.00	50	0.00	N	
Divivy Control	76 Sulvival		100.00	0.00	100.00	0.00	0.00	4	
6.20			0.00	0.00	0.00	0.00		4	
12.5			0.00	0.00	0.00	0.00		4	
25			0.00	0.00	0.00	0.00		4	
50			0.00	0.00	0.00	0.00		4	
100			0.00	0.00	0.00	0.00		4	-
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50			25.00	25.00	25.00	0.00	0.00	1	
100			25.00	25.00	25.00	0.00	0.00	1	-
DMW Control	рН		8.10	8.10	8.10	0.00	0.00	1	
6.25			7.20	7.20	7.20	0.00	0.00	1	
12.5			7.00	7.00	7.00	0.00	0.00	1	
25			6.10	6.10	6.10	0.00	0.00	1	
50			4.20	4.20	4.20	0.00	0.00	1	
100			3.20	3.20	3.20	0.00	0.00	1	_
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	-
6.25			101.00	101.00	101.00	0.00	0.00	1	
12.5			99.60	99.60	99.60	0.00	0.00	1	
25			100.70	100.70	100.70	0.00	0.00	1	
50			101.50	101.50	101.50	0.00	0.00	1	
100			99.80	99.80	99.80	0.00	0.00	1	
DMW Control	Conductivity uS/c	m	171.10	171.10	171.10	0.00	0.00	1	•
6.25	,		362.00	362.00	362.00	0.00	0.00	1	
12.5			529.00	529.00	529.00	0.00	0.00	1	
25			839.00	839.00	839.00	0.00	0.00	1	
50			1437.00	1437.00	1437.00	0.00	0.00	1	
100			2730.00	2730.00	2730.00	0.00	0.00	1	

ToxCalc v5.0.23

			Cerio	odaphnia Surv	vival and Reproduction Test-48 Hr Survival
Start Date:	10/24/2007	17:00	Test ID:	PR0326/04	Sample ID: L12
End Date:	10/26/2007	17:00	Lab ID:	2369	Sample Type: Sediment Elutriate
Sample Date:			Protocol:	ESASOP101	Test Species: CD-Ceriodaphnia dubia
Comments:					
Conc-%	1	2	3	4	
DMW Control	1.0000	1.0000	1.0000	1.0000	
6.25	0.0000	0.0000	0.0000	0.0000	
12.5	0.0000	0.0000	0.0000	0.0000	
25	0.0000	0.0000	0.0000	0.0000	
50	0.0000	0.0000	0.0000	0.0000	
100	0.0000	0.0000	0.0000	0.0000	

		_	Т	Transform: Arcsin Square Root					1-Tailed	
Conc-%	Mean	N-Mean	Mean	Min	Мах	CV%	Ν	Sum	Critical	
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4			
*6.25	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00	
*12.5	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00	
*25	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00	
*50	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00	
*100	0.0000	0.0000	0.2255	0.2255	0.2255	0.000	4	10.00	10.00	

Auxiliary Tests					Statistic	Critical	Skew
Shapiro-Wilk's Test indicates norma	al distribution	(p > 0.01)			1	0.884	
Equality of variance cannot be confi	rmed						
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	τu			
Steel's Many-One Dank Test	<6.25	6.25					



Dose-Response Plot

Page 1

ToxCalc v5.0.23

Reviewed by:

		Ceri	iodaphnia Su	vival and	Reprod	uction Test-4	8 Hr Su	rvival	
Start Date:	10/24/2007 17:00	Test ID:	PR0326/04			Sample ID:		L12	
End Date:	10/26/2007 17:00	Lab ID:	2369			Sample Type	e:	Sediment	Elutriate
Sample Date:		Protocol:	ESASOP101			Test Species	S:	CD-Cerio	daphnia dubia
Comments:									
	_			Au	xiliary Da	ata Summary			_
Conc-%	Parameter		Mean	Min	Max	SD	CV%	N	
DMW Control	% Survival		100.00	100.00	100.00	0.00	0.00	4	
6.25			0.00	0.00	0.00	0.00		4	
12.5			0.00	0.00	0.00	0.00		4	
25			0.00	0.00	0.00	0.00		4	
50			0.00	0.00	0.00	0.00		4	
100			0.00	0.00	0.00	0.00	0.00	4	-
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50			25.00	25.00	25.00	0.00	0.00	1	
100			25.00	25.00	25.00	0.00	0.00	1	-
DMW Control	рн		8.10	8.10	8.10	0.00	0.00	1	
6.25			8.10	8.10	8.10	0.00	0.00	1	
12.5			8.00	8.00	8.00	0.00	0.00	1	
25			8.00	8.00	8.00	0.00	0.00	1	
50			7.80	7.80	7.80	0.00	0.00	1	
100			7.40	7.40	7.40	0.00	0.00	1	-
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	
6.25			102.30	102.30	102.30	0.00	0.00	1	
12.5			101.90	101.90	101.90	0.00	0.00	1	
25			101.80	101.80	101.80	0.00	0.00	1	
50			101.50	101.50	101.50	0.00	0.00	1	
DMW Control	Conductivity US/		98.50	98.50	98.50	0.00	0.00	1	-
E 25	Conductivity US/		186.50	186.50	186.50	0.00	0.00	1	
0.20			201.00	201.00	201.00	0.00	0.00	1	
12.0			201.00	201.00	201.00	0.00	0.00	1	
20			223.00	229.00	223.00	0.00	0.00	1	
100			204.00	204.00	204.00	0.00	0.00	1	

ToxCalc v5.0.23

			Cerie	odaphnia Survival an	d Reproduction Test-48 Hr	Survival
Start Date:	10/24/2007	17:00	Test ID:	PR0326/05	Sample ID:	L15
End Date:	10/26/2007	17:00	Lab ID:	2370	Sample Type:	Sediment Elutriate
Sample Date:			Protocol:	ESASOP101	Test Species:	CD-Ceriodaphnia dubia
Comments:						
Conc-%	1	2	3	4		
DMW Control	1.0000	1.0000	1.0000	1.0000		
6.25	1.0000	1.0000	1.0000	1.0000		
12.5	1.0000	1.0000	1.0000	1.0000		
25	1.0000	1.0000	1.0000	1.0000		
50	1.0000	1.0000	1.0000	1.0000		
100	1.0000	1.0000	1.0000	1.0000		

		_	Т	ransform:	Rank	1-Tailed			
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	Ν	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
6.25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
12.5	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
50	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
100	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00

Auxiliary Tests			Statistic	Critical	Skew		
Shapiro-Wilk's Test indicates norma		1	0.884				
Equality of variance cannot be confi							
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	ΤU			
Steel's Manv-One Rank Test	100	>100		1			



Dose-Response Plot

ToxCalc v5.0.23

Start Date:	10/24/2007 17:00	Toct ID:	DD0206/05	i vivai allu	Reprodu	Sample ID:	o ni Sui	145	
Start Date.	10/24/2007 17:00	Test ID.	PR0326/05			Sample ID.		L10 On dimensión	-1
End Date:	10/26/2007 17:00	Lab ID:	2370			Sample Type	2.	Sediment i	ziutriate
Sample Date:		Protocol.	ESASOPTU	1		rest species		CD-Ceriod	aphnia dubia
Comments.				A	viliam. Dat				
Conc-%	Parameter		Mean	Min	Max	SD	CV%	N	
DMW Control	% Survival		100.00	100.00	100.00	0.00	0.00	4	
6.25			100.00	100.00	100.00	0.00	0.00	4	
12.5			100.00	100.00	100.00	0.00	0.00	4	
25			100.00	100.00	100.00	0.00	0.00	4	
50			100.00	100.00	100.00	0.00	0.00	4	
100			100.00	100.00	100.00	0.00	0.00	4	
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50			25.00	25.00	25.00	0.00	0.00	1	
100			25.00	25.00	25.00	0.00	0.00	1	
DMW Control	pН		8.10	8.10	8.10	0.00	0.00	1	
6.25			7.30	7.30	7.30	0.00	0.00	1	
12.5			7.40	7.40	7.40	0.00	0.00	1	
25			7.50	7.50	7.50	0.00	0.00	1	
50			7.50	7.50	7.50	0.00	0.00	1	
100			7.60	7.60	7.60	0.00	0.00	1	
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	
6.25			103.20	103.20	103.20	0.00	0.00	1	
12.5			102.30	102.30	102.30	0.00	0.00	1	
25			102.00	102.00	102.00	0.00	0.00	1	
50			101.80	101.80	101.80	0.00	0.00	1	
100			100.10	100.10	100.10	0.00	0.00	1	
DMW Control	Conductivity uS/	cm	171.10	171.10	171.10	0.00	0.00	1	
6.25			172.00	172.00	172.00	0.00	0.00	1	
12.5			172.10	172.10	172.10	0.00	0.00	1	
25			172.70	172.70	172.70	0.00	0.00	1	
50			173.80	173.80	173.80	0.00	0.00	1	
100			176.00	176.00	176.00	0.00	0.00	1	

ToxCalc v5.0.23
			Cerie	odaphnia Surv	vival and Reproduction Test-48 Hr Survival	
Start Date:	10/24/2007	17:00	Test ID:	PR0326/06	Sample ID: L16	
End Date:	10/26/2007	17:00	Lab ID:	2371	Sample Type: Sediment Elu	triate
Sample Date:			Protocol:	ESASOP101	Test Species: CD-Ceriodapl	nnia dubia
Comments:						
Conc-%	1	2	3	4		
DMW Control	1.0000	1.0000	1.0000	1.0000		
6.25	1.0000	1.0000	1.0000	1.0000		
12.5	1.0000	1.0000	1.0000	1.0000		
25	1.0000	1.0000	1.0000	1.0000		
50	1.0000	1.0000	1.0000	1.0000		
100	1.0000	1.0000	1.0000	1.0000		

						- /			
		_	TI	ransform:	Arcsin Sq	uare Root		Rank	1-Tailed
Conc-%	Mean	N-Mean	Mean	Min	Max	CV%	Ν	Sum	Critical
DMW Control	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4		
6.25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
12.5	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
25	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
50	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00
100	1.0000	1.0000	1.3453	1.3453	1.3453	0.000	4	18.00	10.00

Auxiliary Tests					Statistic	Critical	Skew
Shapiro-Wilk's Test indicates normal distribution (p > 0.01)					1	0.884	
Equality of variance cannot be confi	irmed						
Hypothesis Test (1-tail, 0.05)	NOEC	LOEC	ChV	τu			
Steel's Many-One Rank Test	100	>100		1			
			-	-			



ToxCalc v5.0.23

Reviewed by:____

		Ceri	odaphnia S	urvival and	d Reprodu	uction Test-	48 Hr Su	rvival	
Start Date:	10/24/2007 17:00	Test ID:	PR0326/06			Sample ID:		L16	
End Date:	10/26/2007 17:00	Lab ID:	2371			Sample Typ	e:	Sediment	Elutriate
Sample Date:		Protocol:	ESASOP10)1		Test Specie	s:	CD-Cerio	daphnia dubia
Comments:									
0	B			Au	Ixiliary Da	ata Summar	/		-
DMW Control	% Survival		100.00	100.00	100.00	SD 0.00	CV%	<u>N</u>	
6 25	76 Sulvival		100.00	100.00	100.00	0.00	0.00	4	
12.5			100.00	100.00	100.00	0.00	0.00	4	
12.0			100.00	100.00	100.00	0.00	0.00	4	
50			100.00	100.00	100.00	0.00	0.00	4	
100			100.00	100.00	100.00	0.00	0.00	4	
DMW Control	Temp C		25.00	25.00	25.00	0.00	0.00	1	-
6.25			25.00	25.00	25.00	0.00	0.00	1	
12.5			25.00	25.00	25.00	0.00	0.00	1	
25			25.00	25.00	25.00	0.00	0.00	1	
50	1		25.00	25.00	25.00	0.00	0.00	1	
100	1		25.00	25.00	25.00	0.00	0.00	1	
DMW Control	pН		8.10	8.10	8.10	0.00	0.00	1	-
6.25			8.10	8.10	8.10	0.00	0.00	1	
12.5			8.10	8.10	8.10	0.00	0.00	1	
25			8.10	8.10	8.10	0.00	0.00	1	
50			8.10	8.10	8.10	0.00	0.00	1	
100			8.00	8.00	8.00	0.00	0.00	1	
DMW Control	DO (% sat)		102.70	102.70	102.70	0.00	0.00	1	_
6.25			101.90	101.90	101.90	0.00	0.00	1	
12.5			101.40	101.40	101.40	0.00	0.00	1	
25	i i i i i i i i i i i i i i i i i i i		101.40	101.40	101.40	0.00	0.00	1	
50	1		100.80	100.80	100.80	0.00	0.00	1	
100			98.00	98.00	98.00	0.00	0.00	1	
DMW Control	Conductivity uS/cn	n	171.10	171.10	171.10	0.00	0.00	1	
6.25			171.80	171.80	171.80	0.00	0.00	1	
12.5			171.90	171.90	171.90	0.00	0.00	1	
25			172.60	172.60	172.60	0.00	0.00	1	
50			1/3.90	1/3.90	1/3.90	0.00	0.00	1	
100			176.60	176.60	176.60	0.00	0.00	1	

ToxCalc v5.0.23

Reviewed by:_____

				Amphipod Sedi	iment Toxicity Te	st-10-day Surv	/ival
Start Date:	10/30/2007	13:00	Test ID:	PR0326/08	Sa	ample ID:	Various
End Date:	11/9/2007 1	13:00	Lab ID:	2366-2371	Sa	ample Type:	Whole Sediment
Sample Date:			Protocol:	ESASOP109	Te	est Species:	CO-Corpohium sp.
Comments:							
Conc-%	1	2	3	4			
Contro	0.9000	0.9000	0.9000	1.0000			
L1	0.7000	0.8000	0.9000	0.6000			
L16	0.9000	0.9000	0.9000	0.9000			
L12	0.0000	0.0000	0.0000	0.0000			
L15	0.7000	0.9000	1.0000	0.7000			
L9	0.0000	0.0000	0.0000	0.0000			
L7	1.0000	0.9000	0.9000	0.8000			

		_	T	ransform:	Arcsin Sq	uare Root		_	1-Tailed	
Conc-%	Mean	N-Mean	Mean	Min	Мах	CV%	Ν	t-Stat	Critical	MSD
Control	0.9250	1.0000	1.2898	1.2490	1.4120	6.318	4			
L1	0.7500	0.8108	1.0584	0.8861	1.2490	14.733	4	2.449	2.490	0.2353
L16	0.9000	0.9730	1.2490	1.2490	1.2490	0.000	4	0.431	2.490	0.2353
L12	0.0000	0.0000	0.1588	0.1588	0.1588	0.000	4			
L15	0.8250	0.8919	1.1608	0.9912	1.4120	17.825	4	1.365	2.490	0.2353
L9	0.0000	0.0000	0.1588	0.1588	0.1588	0.000	4			
L7	0.9000	0.9730	1.2543	1.1071	1.4120	9.935	4	0.375	2.490	0.2353

Auxiliary Tests	Statistic		Critical		Skew
Shapiro-Wilk's Test indicates normal distribution (p > 0.01)	0.939882		0.868		0.37552
Equality of variance cannot be confirmed					
Hypothesis Test (1-tail, 0.05)	MSDu	MSDp	MSB	MSE	F-Prob
Ronferroni t Test indicates no significant differences	0 166794	0 180691	0.034983	0.01786	0 152845



Dose-Response Plot

ToxCalc v5.0.23

Reviewed by:

			Amphipod	Sedimen	t Toxicity	Test-10-day	Survival	<u> </u>	
Start Date:	10/30/2007 13:00	Test ID:	PR0326/08	3		Sample ID:		Various	
End Date:	11/9/2007 13:00	Lab ID:	2366-2371			Sample Typ	e:	Whole Se	ediment
Sample Date:		Protocol:	ESASOP1	09		Test Specie	S:	CO-Corp	ohium sp.
Comments:									
				Α	uxiliary Da	ata Summar	у		_
Conc-%	Parameter		Mean	Min	Мах	SD	CV%	Ν	
Contro	% Survival		92.50	90.00	100.00	5.00	2.42	4	
L1			75.00	60.00	90.00	12.91	4.79	4	
L16	;		90.00	90.00	90.00	0.00	0.00	4	
L12	2		0.00	0.00	0.00	0.00		4	
L15	i		82.50	70.00	100.00	15.00	4.69	4	
LS)		0.00	0.00	0.00	0.00		4	
L7	,		90.00	80.00	100.00	8.16	3.17	4	
Contro	I Temp C		20.00	20.00	20.00	0.00	0.00	1	-
L1	•		20.00	20.00	20.00	0.00	0.00	1	
L16	i		20.00	20.00	20.00	0.00	0.00	1	
L12			20.00	20.00	20.00	0.00	0.00	1	
L15	5		20.00	20.00	20.00	0.00	0.00	1	
LS)		20.00	20.00	20.00	0.00	0.00	1	
 L7			20.00	20.00	20.00	0.00	0.00	1	
Contro	Ha		7.10	7.10	7.10	0.00	0.00	1	-
L1	- F.		7 30	7 30	7 30	0.00	0.00	1	
116			7 30	7 30	7 30	0.00	0.00	1	
112			7 20	7 20	7 20	0.00	0.00	1	
L 15			7.30	7.30	7.30	0.00	0.00	1	
10			3.00	3.00	3.00	0.00	0.00	1	
17			7 20	7 20	7 20	0.00	0.00	1	
Contro	DO (% sat)		100.30	100.30	100.30	0.00	0.00	1	-
L1			99.50	99.50	99.50	0.00	0.00	1	
116			00.00	00.00	00.00	0.00	0.00	1	
142	r		100.40	100.40	100.40	0.00	0.00	4	
115			100.40	100.40	100.40	0.00	0.00	1	
L10			100.30	100.30	100.30	0.00	0.00	4	
1.2			100.70	100.70	100.70	0.00	0.00	1	
L/	O and the first second		100.70	100.70	100.70	0.00	0.00	1	_
Control	Conductivity uS/cn	1	2090.00	2090.00	2090.00	0.00	0.00	1	
L1			249.00	249.00	249.00	0.00	0.00	1	
L16			248.00	248.00	248.00	0.00	0.00	1	
L12			368.00	368.00	368.00	0.00	0.00	1	
L15			246.00	246.00	246.00	0.00	0.00	1	
L9			2330.00	2330.00	2330.00	0.00	0.00	1	
L7			272.00	272.00	272.00	0.00	0.00	1	

Reviewed by:_____

Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



REPORT OF ANALYSIS

Laboratory Reference: A07/3230

Client:	Ecotox Services Australasia Pty Ltd	Order No:	
	Unit 27/2 Chaplin Drive	Project:	Metals Analysis
	Lane Cove NSW 2066	Sample Type:	Water
		No. of Samples:	7
Contact:	Rick Krassoi	Date Received:	27/11/2007
		Date Completed:	30/11/2007

Laboratory Contact Details:

 Client Services
 Manager:
 Attila Tottszer

 Technical Enuries:
 Ian Eckhard

 Telephone:
 +61 2 9888 9077

 Fax:
 +61 2 9888 9577

 Email:
 attila.tottszer@advancedanalytical.com.au

Attached Results Approved By:

lan Eckhard

Technical Director

Comments:

All samples tested as submitted by client. All attached results have been checked and approved for release. This is the Final Report and supersedes any reports previously issued with this batch number. This document is issued in accordance with NATA's accreditation requirements. Accredited for compliance with ISO/IEC 17025. This document shall not be reproduced, except in full.



Issue Date: 3 December 2007 Advanced Analytical Australia Pty ltd ABN 20 105 644 979 11 Julius Avenue, North Ryde NSW 2113 Australia

Page 1 of 3

Ph: +61 2 9888 9077 Fax: +61 2 9888 9577 contact@advancedanalytical.com.au www.advancedanalytical.com.au Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



LaboratoryReference:	-	-	/1	/2	/3	/4
Client Reference:	-	-	Ll	L7	L12	L9
Date Sampled:	-	-	27/11/2007	27/11/2007	27/11/2007	27/11/2007
Analysis Description	Method	Units				
Trace Elements						
Arsenic - Dissolved	04-003	mg/L	<0.02	<0.02	<0.02	<0.02
Cadmium - Dissolved	04-003	mg/L	< 0.001	<0.001	0.11	0.22
Copper - Dissolved	04-003	mg/L	0.002	0.007	0.12	1.6
Lead - Dissolved	04-003	mg/L	< 0.006	<0.006	0.39	2.1
Zinc - Dissolved	04-003	mg/L	<0.003	0.012	0.78	<0.003

Project: Metals Analysis

LaboratoryReference: Client Reference: Date Sampled:			/5 L15 27/11/2007	/6 L16 27/11/2007	/7 Control 27/11/2007
Analysis Description	Method	Units			
Trace Elements					
Arsenic - Dissolved	04-003	mg/L	<0.02	<0.02	<0.02
Cadmium - Dissolved	04-003	mg/L	<0.001	<0.001	<0.001
Copper - Dissolved	04-003	mg/L	0.003	0.002	<0.001
Lead - Dissolved	04-003	mg/L	<0.006	<0.006	<0.006
Zinc - Dissolved	04-003	mg/L	0.003	<0.003	<0.003

Method	Method Description
04-003	Metals by ICP-OES, mg/L

	-
Recult	Commente
CC-Stuar	Comments

Less than

Batch Number: A07/3230

[<] [INS] Insufficient sample for this test [NA] Test not required

Issue Date: 3 December 2007

Advanced Analytical Australia Pty ltd ABN 20 105 644 979 11 Julius Avenue, North Ryde NSW 2113 Australia

Page 2 of 3

Ph: + 61 2 9888 9077 Fax: + 61 2 9888 9577 contact@advancedanalytical.com.au www.advancedanalytical.com.au

Heavy Metals and Metalloids in the Leichhardt River: Lead Pathways Study - Phase 1 (Emissions to Land)



Batch Number: A07/3230

Project: Metals Analysis

QUALITY ASSURANCE REPORT

TEST	Units	Blank	Duplicate Sm#	Duplicate Results	Spike Sm#	Spike Results
Arsenic - Dissolved	mg/L	< 0.004	A07/3230-1	<0.02 <0.02	A07/3230-2	120%
Cadmium - Dissolved	mg/L	< 0.0005	A07/3230-1	<0.001 <0.001	A07/3230-2	109%
Copper - Dissolved	mg/L	< 0.001	A07/3230-1	0.002 0.002 RPD: 0	A07/3230-2	114%
Lead - Dissolved	mg/L	<0.004	A07/3230-1	<0.006 <0.006	A07/3230-2	114%
Zinc - Dissolved	mg/L	<0.003	A07/3230-1	<0.003 <0.003	A07/3230-2	118%

Comments:

RPD = Relative Percent Deviation

[NT] = Not Tested

[N/A] = Not Applicable

= Spike recovery data could not be calculated due to high levels of contaminants

Acceptable replicate reproducibility limit or RPD: Results < 10 times LOR: no limits.

Results between 10 and 20 times LOR: 0% - 50%. Results > 20 times LOR: 0% - 20%.

Recommended matrix spike recovery limits:

Trace elements 75-125% Organic analyses 70-130%

When levels outside these limits are obtained, an investigation into the cause of the deviation is performed before the batch is accepted or rejected, and results are released.

Issue Date: 3 December 2007 Advanced Analytical Australia Pty ltd ABN 20 105 644 979 11 Julius Avenue, North Ryde NSW 2113 Australia Page 3 of 3

Ph: +61 2 9888 9077 Fax: +61 2 9888 9577 contact@advancedanalytical.com.au www.advancedanalytical.com.au

Appendix 5 Summary Report on the completed Leichhardt River Remediation Project Works





Leichhardt River Remediation Project Summary Report

Executive Summary

The Leichhardt River Remediation Project involved the identification and removal of remaining mine sediment material in the Leichhardt River, between Isa Street Bridge at the south and Alma Street Crossing at the north. Although testing demonstrated the health risk to be minimal, the remediation was undertaken to remove any potential risk to the health of residents of Mount Isa from the heavy metal content associated with the sediments.

The remediation project was based on sample results from the Phase 1 (Emission to Land) study of the Lead Pathways study which assessed the performance and effectiveness of remedial works completed between 1991 and 1994 in the Leichhardt River to remove historical mine sediments.

Following a comprehensive depth sampling program, the area requiring removal was determined using a cut off value of 3,000mg/kg for lead in sediments. The cut off value was based on the application of bioaccessibility factors to total concentrations, which was then compared against the NEPM Level E health investigation guidelines.

A total of 120,000 tonnes of material was removed from the Leichhardt River during the project. The contaminated material was disposed of on the Mount Isa Mines lease. 25,000 tonnes of clean rock fill was placed back into the river as rock armouring to prevent erosion.

An ongoing verification program will be followed to allow for any remaining historical mine sediments to be identified and remediated as necessary.

Introduction

Background

Historical mining practices in the 1940s and 1950s resulted in the deposition of mine sediments into the Leichhardt River. Remedial works were completed by MIM Holdings in cooperation with the Mount Isa City Council and the Queensland Government CHEM Unit, between 1991 and 1994, to remove mine sediments in areas adjacent to the town complex and the Leichhardt River.

In the 2005-2010 Mining Plan submitted to and approved by the regulatory body under the *Mount Isa Mines Limited Agreement Act 1985*, Xstrata Mount Isa Mines committed to undertaking an assessment of the Leichhardt River to determine the success of earlier remediation works to remove historical sediments, and to undertake further remedial action if required.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009



The Leichhardt River Remediation Project was initiated based on the results of Phase 1 (Emissions to Land) of the Lead Pathways Study (originally the Whole of Emissions Study). One of the aims of Phase1 (Emissions to Land) was to assess the performance and effectiveness of the remedial works completed between 1991 and 1994.

Lead Pathways Study - Phase 1 (Emissions to Land) Study Results

During the initial Phase 1 study, 21 representative soil and sediment samples were collected from upstream and downstream of the Leichhardt River in Mount Isa. This included samples taken from the vicinity of the velodrome (Wellington Oval), the local swimming pool (Splashez), Kruttschnitt Oval, and the Skate Park. The samples comprised 13 soils, 6 sediments and 2 samples for acid generation properties; their locations are indicated in Appendix A.

Results of the Phase 1 (Emissions to Land) study indicated that previous remediation works to remove historical mine sediments from the river had been very successful. However, natural erosion caused by water movement within the river over time had uncovered additional mine related sediments in some locations. The lead concentrations of historical mine sediments between the Grace Street Bridge and downstream of the velodrome, once adjusted using bioaccessibility factors, showed some exceedances of the NEPM Health Investigation Level E (recreational areas) investigation level. While these locations were considered to be areas of low public activity, the Level E health investigation had been chosen for comparison purposes as a conservative measure.

A human health risk assessment conducted as part of the Phase 1 (Emissions to Land) study determined that the risk presented by these sediments to human health was minimal. Nevertheless, Xstrata Mount Isa Mines committed to the removal of these sediment materials, through the Leichhardt River Remediation Project.

The Leichhardt River Remediation Project (LRRP)

LRRP Stage 1 – Sampling and Quantification

Stage 1 works, conducted in September 2007, involved the use of mobile equipment to dig holes and obtain soil samples at various locations between the Isa Street Bridge to the south and Alma Street Crossing to the north.

The objective of stage 1 of the project was to delineate existing historical mine sediments remaining in the Leichhardt River.

In order to do this a comprehensive sampling program was undertaken which involved:

- sampling at depth along cross sections across the river from west to east;
- taking a total of 152 samples from between Isa Street and upstream of Lake Moondarra;
- supervision by Associate Professor Barry Noller (Centre for Mined Land Rehabilitation); and
- stakeholder interaction with the Mount Isa City Council, Mount Isa Water Board, Queensland Health, Queensland Environmental Protection Agency, Department of

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009



Natural Resources and Water, Department of Mines and Energy, Mount Isa Department of Communities and the Mount Isa Community.

The results of stage 1 determined that the historical mine sediments could be visually identified. Figure 1a&1b show visible historical sediments in profile and on surface.



Figure 1: Historical mine sediments identified for removal a) historical mine sediments within the sediment profile as identified during depth sampling, and b) historical mine sediments with some salting visible on the surface.

LRRP Stage 2 – Remediation works

Stage 2 of the Leichhardt River Remediation Project, conducted in May and June 2008, involved the removal of historical mine sediment to minimise any potential risk to the community from its heavy metal content. The work covered a long stretch of the Leichhardt River from Isa Street Bridge to the south and the Rugby Park to the north. Appendix B shows the areas from which material was removed.

The analysis undertaken in stage 1 was used to determine the boundaries of the areas requiring remediation, including the depth.

Removal was based on the concentration of lead in soil. A material removal trigger value of 3,000mg/kg of lead was used. This was derived by:

- adopting the NEPM health investigation level E (recreational areas) investigation level of 600mg/kg. While the areas have low public activity, level E was adopted as a conservative measure; and
- applying a bioaccessibility factor of 20%, to represent the proportion of the heavy metal content that is capable of being absorbed. This factor was determined based on the bioavailability testing results from the Phase 1 (Emissions to Land) study

Boundaries were modified where necessary during the remediation process to allow for the removal of any visible historical sediment observed outside of the pre-determined areas.

Centre for Mined Land Rehabilitation, The University of Queensland: June 2009



The Leichhardt River Remediation project involved extensive excavation and removal of material utilising heavy mobile equipment such as backhoes, excavators, dozers, trucks and water trucks for dust suppression. The material removed from the Leichhardt River was transported to, and disposed of, on the Mount Isa Mines lease in a safe location.

Where required, benign fill material was used to stabilise banks from encroachment (Figure 2). The bank armouring was designed to target areas likely to be subject to excessive erosion caused by high level flows within the Leichhardt River during the wet season.

A total of 120,000 tonnes of material was removed from the Leichhardt River during the project. 25,000 tonnes of clean rock fill was placed back into the river as rock armouring to prevent erosion.



Figure 2: Rock armoured banks following completion of the Leichhardt River Remediation Project





Figure 3: The Leichhardt River following the completion of the Leichhardt River Remediation Project

Ongoing Evaluation Processes

Following the completion of the Leichhardt River Remediation Project, extensive verification sampling will be undertaken after each wet season until 2011.

Visual surveys will also be intermittently conducted along the river to identify areas displaying visual indicators of material with characteristics similar to that of the historical mine sediments. Any areas of interest identified in the visual surveys will be investigated.

Should verification sampling indicate that there are remaining historical sediments requiring removal, further remediation works will be undertaken.











