The environmental fate of traffic-derived metals in a section of Wet Tropics World Heritage Area (WTWHA), Far North Queensland (FNQ)

Thesis submitted by:

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Abstract

The major aim of this research was to resolve the following question:

What are the key processes affecting the concentrations, mobility and bioavailability of traffic-derived metals (Cd, Cu, Pb, Ni, Zn, Pd and Pt) in roadside environments in a section of the wet-dry tropics in northern Australia?

Specific areas investigated included the Kuranda Range Road, northwest of the city of Cairns; the Captain Cook Highway at the base of the Kuranda Range Road; and adjoining streams and grassed fields. The Kuranda Range Road traverses World Heritage-listed rainforest and the Queensland Department of Main Roads plans to upgrade the road from two lanes to four.

Materials analysed in the study comprised bedrock, road sediments, road runoff waters, stream sediments, roadside topsoils, and grasses. Additionally, background stream sediment, stream water, topsoil and grass samples were collected away from roads.

Geochemical analyses of the road sediments from the Kuranda Range Road revealed variable total metal concentrations (median values: 0.19 mg/kg Cd, 41.7 mg/kg Cu, 53.3 mg/kg Pb, 38.8 mg/kg Ni, 852 mg/kg Zn, 0.035 mg/kg Pd, 0.086 mg/kg Pt). Moreover, the studied road sediments exhibited metal enrichment (Ni excepted) relative to background stream sediments (maximum enrichment factors: Cd 1.8x, Cu 1.5x, Pb 6.8x, Zn 17.3x, Pd 49.5x, Pt 82x). Partial (citrate dithionite) and sequential (as per the method of Tessier et al. 1979) extractions were performed on the road sediments to examine their metal host sites. The results demonstrated that approximately 35 % to 95 % of the sediments' metal content was accommodated by acid ($HF-HNO_3-HClO_4$)-insoluble fractions, likely residual silicates. However, significant ($p<0.01$) positive correlations between the C_{org} and Cd, Cu, Pb and Zn concentrations in the road sediments pointed to metal hosting by an organic source, most likely tyre rubber shreds. The extraction techniques revealed that metals associated with tyre rubber are not readily removed by extraction reagents. Hence, other methods, including correlation analyses between metal concentrations and Al, Mn, Fe and C_{org} values, are necessary to accurately interpret metal hosting within road sediments.

Chemical analyses were performed to evaluate the mobility of Cd, Cu, Pb, Ni and Zn within road runoff waters on the Kuranda Range Road. Maximum Cu, Pb and Zn levels in filtered (<0.45 μm) road runoff waters taken in November 2004 (after a prolonged absence of rainfall) were 8x, 6x and 12x greater than their respective highest values in samples acquired in February 2003 and January 2004 (following heavy rainfall). Such temporal metal distribution data for road runoff waters suggest that large volumes of rainfall in wet-dry tropical regions are capable of mobilising high levels of metals from road surfaces during the initial flushing event (i.e. the 'first flush'). Furthermore, laboratory leaching and ponding experiments conducted on road sediments indicated that a small proportion of the total heavy metal content (<10 %) of road sediments is readily dissolved in distilled water. In the leach tests, aqueous Cd, Cu, Ni and Zn concentrations showed a pronounced 'first flush' effect (i.e. metal values were much higher in the first few samples than in the remaining leachates).

To explore the dispersion of metals from road surfaces, stream sediments from Avondale Creek (intersecting the Kuranda Range Road) were analysed for their total metal contents and Pb isotopic ratios (^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb). The results revealed: a) elevated total Pb (29.6 mg/kg) and Pt (0.025 mg/kg) concentrations in the sediments collected downstream of the road compared to sediments upstream of the road (Pb = 7.3 mg/kg, Pt = 0.006 mg/kg); and b) non-radiogenic Pb isotopic signatures (characteristic of Broken Hill Pb used in petrol) in sediment samples downstream of roads relative to background stream sediments. The results likely reflect contamination of the catchment by road sources.

The verification of metal contamination within Avondale Creek triggered an investigation into the bioavailability of traffic-derived metals. This involved an assessment of the uptake of soil-hosted metals by a grass species (*Melinis repens*), growing adjacent to the Kuranda Range Road. Median total metal concentrations in topsoils collected adjacent to the road were much higher than median total metal values in topsoils taken 5 metres from the road edge. In the *M. repens* grass specimens, Cu, Pb, Ni and especially Zn concentrations were elevated in roots acquired from immediately adjacent to the Kuranda Range Road. *M. repens* clearly has the ability to incorporate high concentrations of trace elements when growing on contaminated roadside soils, particularly Zn and to a lesser degree Cu, Pb and Ni. Additionally, extractions using a DTPA-$CaCl_2$-TEA-HCl (DTPA) solution revealed a significant positive correlation ($p<0.01$) between soil-DTPA and root Zn levels in the roadside *M. repens* samples. This indicates that the DTPA reagent is a rudimentary indicator of Zn to the roots of this grass species. Metal concentrations in *M. repens* samples grown in road sediments as part of a greenhouse experiment, were similar to the values exhibited by the field specimens. Moreover, the metal levels extracted from the road sediments by an EDTA-NH_4HCO_3 solution were commensurate with DTPA-extractable values, indicating that both of these solutions target similar metal fractions in road sediments.

The final research phase examined remediation measures for road runoff waters on the planned Kuranda Range Road Upgrade. A treatment selection process identified dissolved metals as the most significant category of pollutants because of their high lability and potential toxicity. Site constraints, including the close proximity of the road to sensitive water catchments, indicated that at-source pollutant attenuation will be the most effective remediation option for the road upgrade. Thus, existing at-source primary treatment measures (e.g. trash racks); secondary technologies (including sand filters); and tertiary structures (such as biofilters) were identified as the most suitable treatment options for the Kuranda Range Road Upgrade. Few tertiary treatment devices exist for road runoff waters (the StormFilter is an exception). Hence, this research explored the capacity of commonly-available materials, including mushroom compost and bentonite, to remove dissolved metals from road sediment leachates. In laboratory experiments conducted in this project, mushroom compost and bentonite displayed strong capacities to reduce dissolved heavy metal concentrations in road sediment leachates (Pb and Zn removal over 80 %). Both materials were very fast-acting (<5 minutes) in achieving metal attenuation. It is envisaged that these adsorptive materials have the potential to be included into structures (such as sand filter beds) that can achieve tertiary treatment of road runoff waters on the upgraded Kuranda Range Road.

Overall, this research demonstrated that annual wet-dry climate cycles control the concentrations, mobility and bioavailability of traffic-derived metals in roadside corridors in the tropics. Metals accumulate in roadside sediments and soils during the prolonged ‘dry season’ from April to October, and are mobilised by road

runoff waters over the ‘wet season’ (November to March). Mobile metals are bioavailable to organisms living adjacent to roads. Consequently, remediation strategies that can reduce the dispersal of these contaminants into natural environments are important in road design and maintenance in the tropics. The use of adsorptive materials such as bentonite in sand filter beds is presented as one such remediation option.

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Glossary

AAC – Advanced Analytical Centre (locations at Cairns and Townsville)

ADD – Antecedent-dry-day (Han et al. 2005)

ADT – Average daily traffic

AHD – Australian Height datum

ANSTO – Australian Nuclear Science and Technology Organisation

ALS – Australian Laboratory Services Pty Ltd

AMG – Australian Map Grid

Background levels – The range in values representing the normal concentration of a given element in a material under investigation, such as rock, soil, plants and water (Gregorich et al. 2002).

bgs – Below ground surface

Biological availability (bioavailability) – The readiness of a chemical compound or element to be taken up by a living organism (Gregorich et al. 2002).

BOM – Bureau of Meteorology

CDU – Charles Darwin University

CEC – Cation exchange capacity

Colloid – Particles smaller than approximately 1 µm (White 1997).

Complex/ coordination compound – Complexes or coordination compounds generally consist of one or more central atoms or central ions, usually metals, with a number of ions or molecules, called ligands, surrounding them and attached to them (Snoeyink and Jenkins

1980). Complexes may be nonionic, cationic or anionic depending on charges of central ions and ligands (Snoeyink and Jenkins 1980).

Contamination – Refers to circumstances where a substance is present in the environment, but not causing any obvious harm (Alloway and Ayres 1997).

C_{org} – Organic carbon

CSIRO – Commonwealth Scientific and Industrial Research Organisation

DTPA – Diethylenetriaminepentaacetic acid

Dry season – The months between and including April and October in north Queensland.

EDS – Energy dispersive spectrometry

EDTA – Ethylenediaminetetraacetic acid

First flush – The delivery of a disproportionately large load of constituents during the early stages of the runoff hydrograph (Schueler 1987).

Flocculation – The joining of particles through electrostatic forces or van der Vaals' forces (White 1997).

FNQ – Far North Queensland

GBR – Great Barrier Reef

Heavy metals - Heavy metals are those metals, including transition and non-transition metals, possessing densities greater than 6g/cm^3 (Alloway 1995). Relative to the alkali and alkaline metals, heavy metals display high ionisation potentials owing to their strong nuclear charge and, as such, are prone to covalent bonding which leads to the formation of stable complexes and compounds (Parker and Rae 1998). They are commonly classed as potentially toxic to life forms, even in very low concentrations (Siegel 2002). However, Hodson (2004) discourages use of the phrase 'heavy metals' and states that it is a "poor scientific term". This is due to many contradictory definitions for heavy metals, based on density, atomic weight and atomic number (Hodson 2004). Despite the controversy associated with the term, ‘heavy metal’ is used in this project to refer to the metals Cd, Cu, Pb, Ni and Zn.

Humic substances – Naturally occurring complexing agents that are degradation-resistant secondary organic materials (Manahan 1993; Alloway 1995).

ICP-AAS – Inductively coupled plasma atomic absorption spectrometry

ICP-AES – Inductively coupled plasma atomic emission spectrometry

ICP-MS – Inductively coupled plasma mass spectrometry

Mobility – The ability of particles and substances to move, either by random motion or under the influence of fields or forces (Queensland Department of Environment 1998).

Organometallic compounds – Compounds in which the organic portion of the anion is bonded to the metal by a carbon-metal bond (Manahan 1993).

Platinum-group elements (PGEs) – Platinum-group elements include Ir, Os, Pd, Pt, Ru and Rh (Cabri 1981). Like the heavy metals, the PGEs display relatively high ionisation potentials relative to the alkali and alkaline earth metals. The PGEs investigated in this project are Pd and Pt.

Pollution – Pollution describes circumstances where toxic effects of contaminants have been observed (Alloway 1995).

Risk – The probability that an adverse effect will occur in a person, group or ecosystem that is exposed to a particular concentration of a hazardous agent (*HRAMCS* 1996) (The Health Risk Assessment and Management of Contaminated Sites).

Roadside corridors/environments – Environments immediately adjacent to roads.

RPD – Relative percent difference

rpm – Revolutions per minute

SEM – Scanning electron microscopy

$S_{sulfate}$ – Sulfate sulfur

$S_{sulfide}$ – Sulfide sulfur

TEA – Triethanolamine

TIMS – Thermal ionisation mass spectrometry

TOC – Total organic carbon

Topsoils – The 0-10cm soil layer below the Earth’s surface. Commonly includes the O, A and B soil horizons which host a mixture of primary and secondary minerals as well as decaying organic matter and degradation-resistant humic compounds (Alloway 1995; Siegel 2002).

Toxicity – The quality or degree of being poisonous or harmful to plant, animal or human life (Queensland Department of Environment 1998).

Treatment train – A number of measures used in sequence to remediate storm and road runoff waters (Melbourne Water 2005).

Wet season – The months between and including November and March in north Queensland.

Wt % – Weight percent

WTWHA – The Wet Tropics World Heritage Area, located adjacent to the North Queensland coastline.

XRD – X-ray diffraction

XRF – X-ray fluorescence

Chapter 1 Project Introduction

1.1 Natural abundance of metals

1.1.1 Introduction

Heavy metals and PGEs are naturally-occurring components of the Earth's crust. These metals are cycled within surficial environments from crustal material that is exposed at the Earth's surface and are included in soil minerals as a result of weathering of parent rock sources (Parker and Rae 1998; Siegel 2002).

Metals which are tightly bound within primary mineral phases are strongly resistant to weathering. However, metals associated with minerals that are highly reactive at the Earth's surface are readily redistributed in soils. Once released from their parent rock matrix by natural weathering processes, metals are distributed in the environment according to local prevailing environmental conditions (Siegel 2002). Consequently, soil, sediments, vegetation and water bodies are all sinks for crustal-derived metals (Siegel 2002).

1.1.2 Crustal abundance

Heavy metals display considerable variation in their crustal abundance. Iron, for example, comprises a significant weight percent of both continental (1 – 2 %) and oceanic (5 – 10 %) crust (Siegel 2002). In comparison, the average crustal concentration of Cd is extremely low (0.1 – 0.2 mg/kg) (Siegel 2002). With few exceptions, notably Fe, heavy metals are generally present in trace amounts (less than 1000 mg/kg, Thakur et al., 2004) in the Earth's crust; hence their common classification as 'trace metals' (Monaci and Bargagli 1997; Utsunomiya et al. 2004).

The crustal abundances of PGEs are even sparser than heavy metals. In fact, the cumulative concentration of all of the PGEs in the Earth's crust totals approximately 1 µg/kg (Zereini and Alt 2000).

Table 1-1 presents published average crustal abundances of individual metals. It can be seen that different rock types host varying metal concentrations. For example, shales and basalts commonly display higher metal values than granites and sandstones. Hence, due to differences in bedrock compositions, there are considerable variations of crustal metal abundances on a regional and local scale (Faure 1991).

Table 1-1: Average crustal abundances of metals studied in the project (^{1} from Berkman 1995, ^{2} from Smith and Huyck 2004). The average concentrations of the metals in various rock types are also shown (from Faure 1991). All values are in mg/kg. NV = no value given.

	Cd	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**
Average crustal abundance^1	0.2	55	12.5	75	70	0.004	0.002
Average crustal abundance^2	0.18	60	16	80	70	0.01	0.005
Granite	0.13	30	15	15	60	NV	NV
Basalt	0.21	94	7	145	118	NV	NV
Shale	0.3	45	20	68	95	NV	NV
Sandstone	NV	NV	7	2	16	NV	NV

1.1.3 Pedosphere

Soils are short-term repositories for metals released from primary rock-forming minerals. Different soil types develop on a wide variety of parent rock material; hence the metal content of these soils varies depending on the metal content of the parent rock (Faure 1991). Published data for average soil metal concentrations are displayed in Table 1-2 and it can be seen that the values show wide ranges. These large concentration variations are due to differences in parent rock compositions and anthropogenic inputs (Smith and Huyck 2004).

Table 1-2: Average concentrations of metals in soils (^{1} from Berkman 1995, ^{2} from Smith and Huyck 2004). All results are presented in mg/kg.

	Cd	**Cu**	**Pb**	**Ni**	**Zn**
Concentration range in soils^1	1	2 - 100	2 - 200	5 - 500	10 - 300
Average values in soils^2	0.06	30	10	40	50

Soils form under varying conditions and consequently display a range of chemical and physical properties. These properties (the most important being cation exchange capacity, soil pH and organic carbon) influence the soil's ability to retain metals released from parent rock material as well as degraded biological matter. Soil cation exchange capacity (CEC) is a measure of the adsorbed cation charge on the surface of the soil particles (White 1997). Generally, the higher the CEC for a soil, the greater its ability to adsorb cations present in soil pore-water solution (White 1997). By comparison, low soil-pH values generally dictate that soil-hosted metals are mobile and may be readily available for uptake by plants (White 1997).

Soil organic carbon (C_{org}) is a good indicator of soil organic matter, which possesses a strong capacity to bind metals (Tada and Suzuki 1982; Parker and Rae 1998; Sauve et al. 2003). Degradation-resistant organic matter, referred to as humic material, is prevalent in topsoil layers. Moreover, humic compounds are capable of forming stable metal complexes, although in many instances these complexes may be more mobile than the uncomplexed metal cations (Parker and Rae 1998).

In addition to soil organic matter, secondary soil mineral constituents (broadly categorised as clays, oxides/oxyhydroxides and carbonates) play a critical role in the sequestration of metals released from their parent rock material. Metals may be highly mobile in soil pore waters, either through dissolution or adsorption to colloidal phases. Oxides/oxyhydroxides, and to a lesser extent clays and carbonates, are effective adsorbers of these mobile metals owing to the significant complexing potential of the edge faces of these minerals (Parker and Rae 1998; Siegel 2002).

1.1.4 Biosphere

Metals may enter the biosphere when they are taken up as dissolved/complexed species by aquatic organisms which have filter-feeding mechanisms (Sures et al. 2003). Furthermore, metals sequestered by soils are potentially incorporated into the biosphere (Siegel 2002), as they are liable for uptake by soil-dwelling plants, fungi, bacteria and soil-feeding invertebrates (Faure 1991).

Additionally, plant root systems are significant pumps for soil-hosted nutrients, which include metals that are essential for cellular processes (e.g. Cu and Zn). However, metals which have no known benefit to living organisms, such as Cd and Pb, are also taken up by plant roots (Manahan 1993). Metal concentrations in plant tissue are extremely variable owing primarily to the differences in physiology between plant species. Within species, local soil and climatic conditions cause further variations in plant tissue metal concentrations between individual specimens (Faure 1991). Ultimately, all metals that are incorporated into living tissue are directed up the food-chain as plants are grazed by herbivores which are in turn consumed by carnivores (Larison et al. 2000).

1.1.5 Surface waters and sediments

Metals weathered from parent rocks may be transported by physical and chemical processes into lakes, streams and ultimately oceans where their partitioning between solid and liquid phases depends on local aqueous chemical conditions. Generally, metals are soluble in waters with low pH and high Eh (oxic) values but are insoluble in high pH and anoxic waters (Munk and Faure 2004). However, even under increasing pH and decreasing Eh, metals may still be highly mobile in surface water bodies as they are adsorbed onto colloids (Parker and Rae 1998).

Stream and lake bed sediments contain adsorptive secondary minerals and organic matter which scavenge dissolved and colloidal metals from overlying waters (Parker and Rae 1998). Therefore, stream and lake bed sediments represent important sinks for metals released from rocks and soils (Tada and Suzuki 1982; Sutherland 2000; Bordas and Bourg 2001).

1.1.6 Significance of understanding the natural distribution of metals

The distribution of heavy metals and PGEs in surficial environments is extremely variable due the factors described in Sections 1.1.1 to 1.1.5. It can be seen that local concentrations of these metals may be enriched through rock-forming mechanisms as well as by subsequent chemical and physical environmental processes at the Earth’s surface. Knowledge of the natural factors influencing heavy metal and PGE distribution in local environments allows for a very important estimation: the understanding of anthropogenic influences on the local distribution and enrichment of these metals in soils, sediments and waters.

1.2 Current knowledge on traffic-derived metal contamination

1.2.1 Introduction

Additional to natural processes, anthropogenic activities may enhance local abundances of heavy metals and PGEs in surficial environments (Parker and Rae 1998; Zereini and Alt 2000). The diffuse release of heavy metals and PGEs into roadside corridors has received increasing attention in recent years.

Motorised vehicles contribute metals to the immediate roadside environment. Cadmium, Cu, Pb, Ni and Zn belong to a group of metals which feature prominently in literature dealing with roadside contamination. Sources of these particular contaminants derived from motor vehicles include: a) engines and brake pads (Cd, Cu, Pb, Ni and Zn) (Sansalone and Buchberger 1997; Viklander 1998); b) lubricants (Cd, Cu and Zn) (Birch and Scollen 2003); c) exhaust emissions (Pb) (Gulson et al. 1981; Al-Chalabi and Hawker 2000; Sutherland et al. 2003); and d) tyres (Cd, Cu, Pb, Ni and Zn) (Fergusson and Kim 1991; Viklander 1998; Smolders and Degryse 2002). Weathering of road infrastructure, such as sign posts and galvanised railings, and road paving materials have also been documented to further contribute heavy metal loadings to roadside corridors (Van-Rooy 1991; Smolders and Degryse 2002). Moreover, since the equipment of some vehicles with catalytic converters over the past 20 years, Pd, Pt and Rh have been continually released into roadside environments due to abrasion within these vehicular components (Zereini and Alt 2000).

1.2.2 Metal contamination on road surfaces

Sediments that settle on road surfaces and in gutters along road edges are an immediate sink for traffic-derived metal contaminants (Birch and Scollen 2003).

The accumulation of heavy metals and PGEs in road sediments has been well-documented by a number of authors, and the details of the studies are presented in Table 1-3.

Table 1-3: Summary of studies which have examined total metal concentrations in road sediments.

Study location	Author	Extractant used	Metals analysed and maximum values (mg/kg)	Particle-size range of road sediment analysed
London, UK	(Harrison et al. 1981)	$HCl-HNO_3-HClO_4-HF$	Cd 2.68, Cu 108, Pb 2100, Zn 539	<600 µm
New York, USA; London, UK; Halifax, Canada; Christchurch, New Zealand; Kingston, Jamaica	(Fergusson and Ryan 1984)	$HClO_4-HF$	Cd 1.4, Cu 233, Pb 2807, Zn 477	<963 µm
Cuenca, Ecuador	(Hewitt and Candy 1990)	HNO_3	Cd 0.42, Pb 970, Zn 1018	<200 µm
Worldwide	(Fergusson and Kim 1991)	$HF-HClO_4$	Cd 396, Pb 74400	Not specified
Sweden	(Viklander 1998)	HNO_3	Cd 0.38 (500 – 250 µm), Cu 240 (<75 µm), Pb 75 (<75 µm), Zn 250 (<75 µm)	4000-200 µm, 2000-1000µm, 1000-500µm, 500-250µm, 250-125 µm, 125-75 µm, <75 µm
Caracas Valley, Venezuela	(Fernandez and Galarraga 2001)	$HCl-HNO_3$ -HF	Pb 5500	Not sieved
Honolulu, USA	(Sutherland and Tolosa 2001)	$HCl-HNO_3-HClO_4-HF$	Pb 280, Zn 500	<2000 µm
West central Scotland	(Higney et al. 2002)	NiS fire assay digest	Pt 0.335	<2000 µm
Sydney, Australia	(Birch and Scollen 2003)	*Aqua regia*	Cu 867, Pb 1999 , Ni 82, Zn 1588	<2000 µm
Amman, Jordan	(Jiries 2003)	HNO_3	Cd 2.50, Cu 600, Ni 42.45, Pb 1925, Zn 675	Not specified
Northern Spain	(Ordonez et al. 2003)	$HCl-HNO_3$	Cd 22.3, Zn 4982	<147 µm
E-5 Highway, Istanbul, Turkey	(Sezgin et al. 2003)	HNO_3	Cd 4.30, Cu 1358.5, Pb 555.4, Zn 1502.5	<500 µm
Honolulu, USA	(Sutherland 2003)	$HCl-HNO_3$	Pt 0.160	<2000 µm
Perth, Australia	(Whiteley 2005)	*Aqua regia*	Pd 0.440, Pt 0.440	<63 µm

In contrast, fewer researchers have examined labile metal fractions hosted by road sediments, commonly through the use of partial extractions (which target specific metal fractions) or sequential extractions (which release progressively more stable metal fractions from sediments) (Table 1-4). These studies have shown that significant amounts of metals are liberated from road sediments by mild extraction reagents (e.g. 0.5 M HCl). The recognition of labile metal proportions is a critical aspect in the study of roadside pollution that cannot be achieved by studies which simply present the total metal concentrations of road sediments. Hence, it is important to gauge the mobility of metals on road surfaces.

Table 1-4: Summary of investigations into labile fractions of metals hosted by road sediments.

Study location	**Author**	**Metals analysed**	**Type of extraction**	**Extraction reagents used**
London, UK	(Harrison et al. 1981)	Cd, Cu, Pb and Zn	Sequential	1 M $MgCl_2$, 1 M NaOAc, 0.04 M NH_2OHHCl – 25 % acetic acid, 0.02 M HNO_3 – 30 % H_2O_2 – 3.2 M NH_4OAc – 20 % HNO_3, HNO_3-HF-HCl-$HClO_4$
New York, USA; London, UK; Halifax, Canada; Christchurch, New Zealand; Kingston, Jamaica	(Fergusson and Ryan 1984)	Cd, Cu, Pb, Zn	Sequential	1 M $MgCl_2$, 1 M NaOAc, 0.04 M NH_2OHHCl – 25 % acetic acid, 0.02 M HNO_3 – 30 % H_2O_2 – 3.2 M NH_4OAc – 20 % HNO_3, HNO_3-HF-HCl-$HClO_4$
Greenwich, UK	(Serrano-Belles and Leharne 1997)	Pb	Partial	0.001 M HCl
Hong Kong	(Wang et al. 1998)	Cu, Pb, Zn	Sequential	1 M $MgCl_2$, 1 M NaOAc, 0.04 M NH_2OHHCl – 25 % acetic acid, 0.02 M HNO_3 – 30 % H_2O_2 – 3.2 M NH_4OAc – 20 % HNO_3, Aqua regia
Honolulu, USA	(Sutherland and Tolosa 2001)	Cu, Pb, Zn	Partial	0.5 M HCl
Honolulu, USA	(Sutherland 2002)	Cu, Pb, Ni, Zn	Partial	0.5 M HCl
Sydney, Australia	(Birch and Scollen 2003)	Cu, Pb, Ni, Zn	Partial	0.05 M EDTA, 1 M HCl
Honolulu, USA	(Sutherland et al. 2004)	Cu, Pb, Ni, Zn	Partial	Acetic acid, EDTA, cold and hot 0.5 M HCl, BCR 2-step, BCR Labile, EPA 3050, Nitric/HCl, BCR 4 step

1.2.3 Metal mobility in road runoff waters

The mobility of Cd, Cu, Pb, Ni and Zn in road runoff waters have been examined by several researchers, and a summary of these studies is presented in Table 1-5. Results from these investigations indicate that elevated metal levels (above background stream concentrations) are mobilised as dissolved and suspended colloidal phases in 'first flush' road runoff waters. These 'first flush' waters are defined as accommodating "the delivery of a disproportionately large mass of a constituent during the early portion of the runoff hydrograph" (Schueler 1987). In other words, 'first flush' waters are those that flow over road surfaces during the initial stages of a significant rainfall event. These waters commonly carry exceptionally high metal concentrations and masses (Sansalone and Buchberger 1997). Cadmium, Cu and Zn have been demonstrated to exhibit high dissolved values in road runoff waters (Sansalone and Buchberger 1997). In contrast, Pb and to a lesser extent Ni have been reported to exhibit low dissolved levels in road runoff waters (Sansalone and Buchberger 1997).

Metals transported by road runoff waters enter the local stormwater system (Rose et al. 2001). Ultimately, they leach into topsoils (Dierkes and Geiger 1999) or are delivered to surface water bodies such as streams and lakes (de-Vos et al. 2002), where they may be redistributed according to local prevailing chemical conditions.

Table 1-5: Summary of investigations researching metal concentrations in road runoff waters.

Study location	Author	Maximum metal concentrations (μg/L)	
		Filtered samples (<0.45 μm)	***Unfiltered samples***
Washington State, USA	(Bourcier 1979)		Pb 1.86, 19.1
Birmingham, UK	(Pitt et al. 1995)	Cu 11, Pb 3.9, Zn 76	Cu 1250, Pb 150, Ni 70, Zn 130
Gold Coast, Brisbane and Sydney, Australia	(Drapper et al. 1997)		Cd 4.9, Cu 327, Pb 500, Ni 2, Zn 1700
Cincinnati, USA	(Sansalone and Buchberger 1997)	Cd 9, Cu 279, Pb 21, Zn 14786	Cd 32, Cu 325, Pb 1457, Zn 15244
Atlanta, USA	(Rose et al. 2001)	Cu 16.9, Pb 11.4, Ni 4.99, Zn 4019	
Sweden	(Backstrom et al. 2003)	Cd 0.26, Cu 60, Pb 3, Zn 100	Cd 0.27, Cu 66, Pb 18, Zn 180
Brisbane, Australia	(Toomey et al. 2003)		Cu 260, Pb 430, Zn 1400
UK	(Muhammad et al. 2004)		Cu 429, Pb 720, Zn 1699
Central Italy	(Mangani et al. 2005)	Cu 86, Pb 3.77, Zn 132.95	Cu 588, Pb 277.46, Zn 2930

1.2.4 Metals in roadside soils

Roadside soils represent an important sink for traffic-derived metals (Sutherland and Tolosa 2001). Soils host a wide variety of adsorptive substances (such as clays and organic matter) which are able to sequester metals that are released from motor vehicles, road infrastructure and road paving materials (Harrison et al. 1981; Turner et al. 2001; Turner and Maynard 2003). Metals may be deposited in roadside soils during dry weather as fine dust or exhaust particles (Birch and Scollen 2003). Additionally, metals can be dispersed into road edge soils by road runoff waters (Sansalone and Buchberger 1997). This process is particularly important in wet-dry tropical environments.

The distribution of traffic-derived metals (Cd, Cu, Pb, Ni, Zn, Pd and Pt) in roadside soils has been researched in various locations worldwide (refer to Table 1-6). The studies indicate that, on a lateral scale, heavy metal and PGE contaminants are most concentrated in a 25 metre zone extending from road edges. On a vertical scale, contamination is commonly restricted to the topsoil layers to a depth of approximately 5 cm bgs (Turner and Maynard 2003). Organic matter has been shown to be critical in restricting traffic-derived metals to the upper few centimetres of roadside topsoils (Turner and Maynard 2003).

Research has also been conducted on the long-range dispersal of traffic-derived metals; namely Pb. Lead isotopic ratios have been used to assess soil contamination by traffic-derived Pb, well away from roads (Gulson et al. 1981). The theory underpinning the use of Pb isotopes in environmental studies stems from the fact that three of the four Pb isotopes are radiogenic and their abundances are continually increasing at a steady rate over time (Ault et al. 1970). For this reason, anthropogenic Pb derived from orebodies that have ‘locked in’ a characteristic Pb isotopic signature at the time of their formation, commonly displays Pb isotopic ratios distinctive from younger soils (Cumming and Richards 1975). The use of Pb isotopic ratios as markers of contamination is discussed in detail in Chapter 5. In a study conducted by Gulson et al. (1981), Pb with a strongly anthropogenic signature (i.e. non-radiogenic Pb) was determined in topsoils in South Australia, up to 50 kms from any major roads. The anthropogenic Pb was interpreted to be derived from petrol exhaust, as no other sources could be reasonably identified in the region (Gulson et al. 1981). These results indicate that metals emitted as fine dust particles (e.g. Pb, Pt and Pd) from road environments may be dispersed great distances from their source.

Table 1-6: Summary of research into metal distributions in roadside soils (<25 m from the road edge).

Study location	Author	Metals analysed and concentrations (mg/kg)
Brisbane, Australia	(Wylie and Bell 1973)	Maximum value – Pb 145
Heirisson Island, WA, Australia	(Bottomley and Boujos 1975)	Maximum value – Pb 80
Hume Hwy, NSW, Australia	(David and Williams 1975)	Maximum values – Cd 0.57, Cu 1.53, Pb 12.4, Zn 29.3
Central North Island, New Zealand	(Ward et al. 1975)	Maximum value – Pb 175
Victoria, Australia	(Clift et al. 1983)	Mean value – Pb 45
Germany	(Weigmann 1991)	Mean values – Cd 0.83, Cu 70, Pb 236
Northwest Spain	(Marino et al. 1992)	Maximum values – Cd 0.75, Cu 150, Pb 116.7, Zn 147.3
Dortmund, Germany	(Münch 1992)	Range of values – Cd 0.6 to 1.4, Pb 48 to 130, Zn 58 to 330
Greece	(Cook et al. 1994)	Mean values – Cu 210, Pb 620, Zn 590
France	(Piron-Frenet et al. 1994)	Maximum value – Pb 643
Tampa, USA	(Hafen and Brinkmann 1996)	Median value – Pb 350
Ibadan, Nigeria	(Olajire and Ayodele 1997)	Mean values – Cd 2.70, Cu 80.5, Pb 730, Ni 115, Zn 213
Lucknow, India	(Singh et al. 1997)	Maximum value – Pb 60
Gipuzkoa, Spain	(Garcia and Millan 1998)	Maximum values – Cd 2.22, Pb 1548, Zn 2204
Germany	(Schafer and Puchelt 1998)	Maximum value – Cu 925, Pb 1000, Zn 1200, Pt 0.25
Southwest Germany	(Hoffmann et al. 1999)	Used magnetic susceptibility values to infer metal concentrations
Amman, Jordan	(Jaradat and Momani 1999)	Mean values – Cd 0.75, Cu 29.7, Pb 188.8, Zn 121.7
Slovenia	(Zupancic 1999)	Maximum value – Pb 1000
Brisbane, Australia	(Al-Chalabi and Hawker 2000)	Mean value – Pb 2910
Honolulu, USA	(Sutherland et al. 2000)	Median value – Cu 118, Pb 56, Ni 286, Zn 230
Cincinnati, USA	(Turner et al. 2001)	Maximum values – Pb 1980, Zn 1430
Oslo, Norway	(Tijhuis et al. 2002)	Median values – Cd 0.34, Cu 23.5, Pb 33.9, Ni 24.1, Zn 130
Osogbo, Nigeria	(Fakayode and Olu-Owolabi 2003)	Mean values – Cd 0.76, Cu 28, Pb 92, Ni 9.65, Zn 56.27
Honolulu, USA	(Sutherland 2003)	Median value – Pt 0.014
West Bank, Palestine	(Swaileh et al. 2004)	Mean values – Cd 0.27, Cu 60.4, Pb 87.4, Ni 18.9, Zn 82.2
Lagos, Nigeria	(Awofolu 2005)	Range of values – Cd 0.01 to 0.12, Cu 0.1 to 2.9, Pb 0.02 to 0.23, Zn 0.51 to 335

1.2.5 Bioavailability of traffic-derived metals

The bioavailability of Cd, Cu, Pb, Ni and Zn in roadside topsoils has also been investigated by a number of researchers (Table 1-7). These studies have shown that high proportions of traffic-derived heavy metals that accumulate in roadside soils are taken up by plants and soil-dwelling organisms (Table 1-7). However, there is yet to be a study which conclusively links roadside metal contamination with toxicity in organisms.

Table 1-7: Synthesis of research into bioavailability of metals in roadside soils.

Study location	**Author**	**Type of organism studied**	**Metals analysed and concentrations (mg/kg relative to dry weight of tissue)**
Brisbane, Australia	(Wylie and Bell 1973)	Plants	Maximum value – Pb 64
Hume Hwy, NSW, Australia	(David and Williams 1975)	Crops and bracken	Maximum values – Cd 0.065, Cu 4.8, Pb 19.1, Zn 84
Central North Island, New Zealand	(Ward et al. 1975)	Plants	Maximum value – Pb 1200
Illinois, USA	(Wheeler and Rolfe 1979)	Plants	Maximum value – Pb 196
Germany	(Weigmann 1991)	Earthworms, centipedes	Maximum values – Cd 10, Cu 13, Pb 130
Northwest Spain	(Marino et al. 1992)	Earthworms	Maximum values – Cd 4.03, Cu 44.64, Pb 70.65, Zn 850.1
Greece	(Cook et al. 1994)	Shrub leaves	Mean values – Cu 57, Pb 85, Zn 130
Ibadan, Nigeria	(Olajire and Ayodele 1997)	Unspecified grass sp.	Mean values – Cd 0.18, Cu 8.94, Pb 205, Ni 10.9, Zn 43.5
Siena, Italy	(Monaci and Bargagli 1997)	Plants	Maximum values – Cd 0.05, Cu, 15.8, Pb 25.2, Ni 1.45, Zn 41.8
Lucknow, India	(Singh et al. 1997)	Grasses, rice plants	Maximum value – Pb (root) 29.37, Pb (stem) 27.94, Pb (leaf) 22.76
Gipuzkoa, Spain	(Garcia and Millan 1998)	Grasses	Maximum values – Cd 0.64, Cu 19.3, Pb 11.7, Zn 130
Amman, Jordan	(Jaradat and Momani 1999)	Plant leaves	Mean values – Cu 31.3, Pb 7.3, Zn 98.7
Croatia	(Blanusa et al. 2002)	Woodlice	Mean values – Cd 0.411, Pb 4.22
West Bank, Palestine	(Swaileh et al. 2004)	Plant leaves	Mean values – Cd 0.1, Cu 10.6, Pb 7.25, Ni 4.87, Zn 47.6
Lagos, Nigeria	(Awofolu 2005)	Grass sp.	Range of values – Cd 0.01 to 0.07, Cu 0.1 to 1.48, Pb 0.01 to 0.14, Zn 0.19 to 1.80

The bioavailability of PGEs has received considerably less focus than that of heavy metals. This is undoubtedly due to the extremely sensitive and costly analytical techniques required for their detection in plant and animal tissue. Because of this, studies into the bioavailability of PGEs have commonly employed experimental studies that monitor the uptake of PGEs from spiked solutions (commonly involving the addition of road sediments to distilled water). Results of these experiments presented in the literature have shown that road sediment-hosted PGEs are available for uptake by aquatic invertebrates and vertebrates (Table 1-8).

Table 1-8: Summary of experimental studies into bioavailability of PGEs.

Author	Type of organism studied	Mean metal values in road dusts (μg/kg)	Mean metal values in organisms (μg/kg relative to dry weight of tissue)
(Sures et al. 2001)	European eels	Pd 21.3	Pd 0.18
(Sures et al. 2002)	Mussels	Pd 29, Pt 244	Pd 3.25, Pt 1.5
(Sures et al. 2003)	Acanthocephalans (fish parasites)	Not given	Pt 3.11

1.2.6 Remediation of metals from road runoff waters

As a result of the documentation of metal uptake by organisms in roadside environments, treatment measures have been developed for road runoff waters which transport labile metals. Storm and road runoff waters transport various contaminants. Numerous treatment options currently exist for storm and road runoff waters. However, new remediation technologies are continually being explored due to the great diversity in the physical and environmental features of roadside environments.

A range of primary and secondary treatment measures have been devised to remove gross pollutants and suspended solids from storm and road runoff waters. Moreover, tertiary remediation measures have been developed to target dissolved metals and other dissolved materials (e.g. pesticides) in road runoff waters. Examples of tertiary treatment structures include constructed wetlands (Toomey et al. 2003), grassed embankments (Barrett et al. 1995) and detention ponds (Lee et al. 1997).

Few studies, however, have focused on treating contaminated road runoff waters at their source; i.e. within road drainage culverts. For example, a peat filtration layer was trialled by Zhou et al. (2003) to lower Zn values in road runoff waters in Tennessee, USA. The layer was shown to sequester over 80 % of Zn from the waters. Additionally, Lau et al. (2000) demonstrated that a biofilter inserted in road drains can remove over 85 % of dissolved Pb and Zn from road runoff waters.

1.2.7 Previous research within the study area

This project focuses on the distributions and concentrations of traffic-derived metals within the Cairns region, in northern Australia. Only two investigations into metal contamination in roadside corridors have been conducted in the Cairns area (Diprose 1999; Williams 2000). These recent studies by James Cook University Honours students examined total heavy metal concentrations in road sediments and roadside topsoils along the Kuranda Range Road (Diprose 1999) and in roadside topsoils alongside sections of the urban Bruce Highway in Cairns (Williams 2000).

1.2.7.1 Total metal values in roadside topsoils

Findings of Diprose (1999) indicated minor contamination in roadside topsoils by Pb, which displayed an average enrichment of approximately 5x compared with background topsoil values. Copper and Zn levels were marginally enriched in the roadside topsoils while Cd and Ni showed no enrichment in the roadside topsoils relative to the background topsoils (Diprose 1999) (Table 1-9).

Table 1-9: Heavy metals in roadside topsoils compared with background topsoils on the Kuranda Range (from Diprose, 1999).

The investigation conducted by Williams (2000) indicated the occurrence of heavy metal contamination of roadside topsoils (<4 m from the road edge) in the urban Cairns area. Lead concentrations were particularly elevated (1200 mg/kg) in topsoils adjacent to the Bruce Highway in Cairns (Williams 2000). Williams (2000) also completed laboratory experiments using extraction agents (namely 1M HCl) to assess the bioavailability of these heavy metal contaminants in roadside topsoils. The experiments indicated that only a minor portion of the metal levels were bioavailable (<10 % of the total metal content of the soils). However, no samples of biological material from the road edge environment were analysed to consolidate these findings.

1.2.7.2 Dispersion of heavy metals from road edges

Results of Diprose (1999) revealed a mild decreasing trend in heavy metal values in topsoils with increasing distance away from the edge of the Kuranda Range Road. Transect locations are shown in Figure 1-1a and b, while total metal concentrations are presented in Figure 1-2a and b. In contrast, within the Cairns area, heavy metal concentrations fell sharply in topsoils collected more than 5 metres from the road edge (Williams 2000). Transect locations from Williams's (2000) study are displayed in Figure 1-1c, and heavy metal values are given in Figure 1-2c. Results of Diprose (1999) showed that topsoil Pb values (0 – 10 cm bgs) were markedly higher than in subsoils (>10 cm bgs) collected adjacent to the Kuranda Range Road. This indicates that these roadside topsoils act as filters inhibiting the vertical migration of Pb.

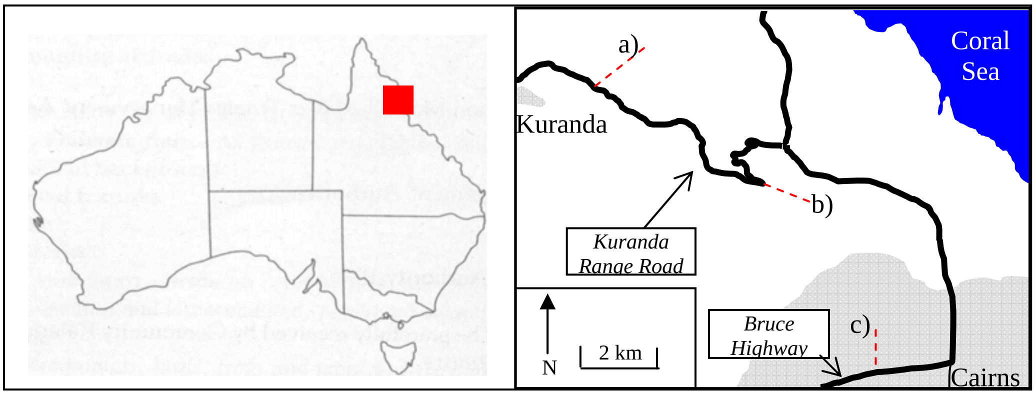

Figure 1-1: Transect locations: a) the edge of the Kuranda Range Road, upper section; b) the edge of the Kuranda Range Road, middle section (from Diprose 1999); and c) the edge of the Bruce Highway in Cairns (from Williams 2000). Scales of the transect lengths are exaggerated.

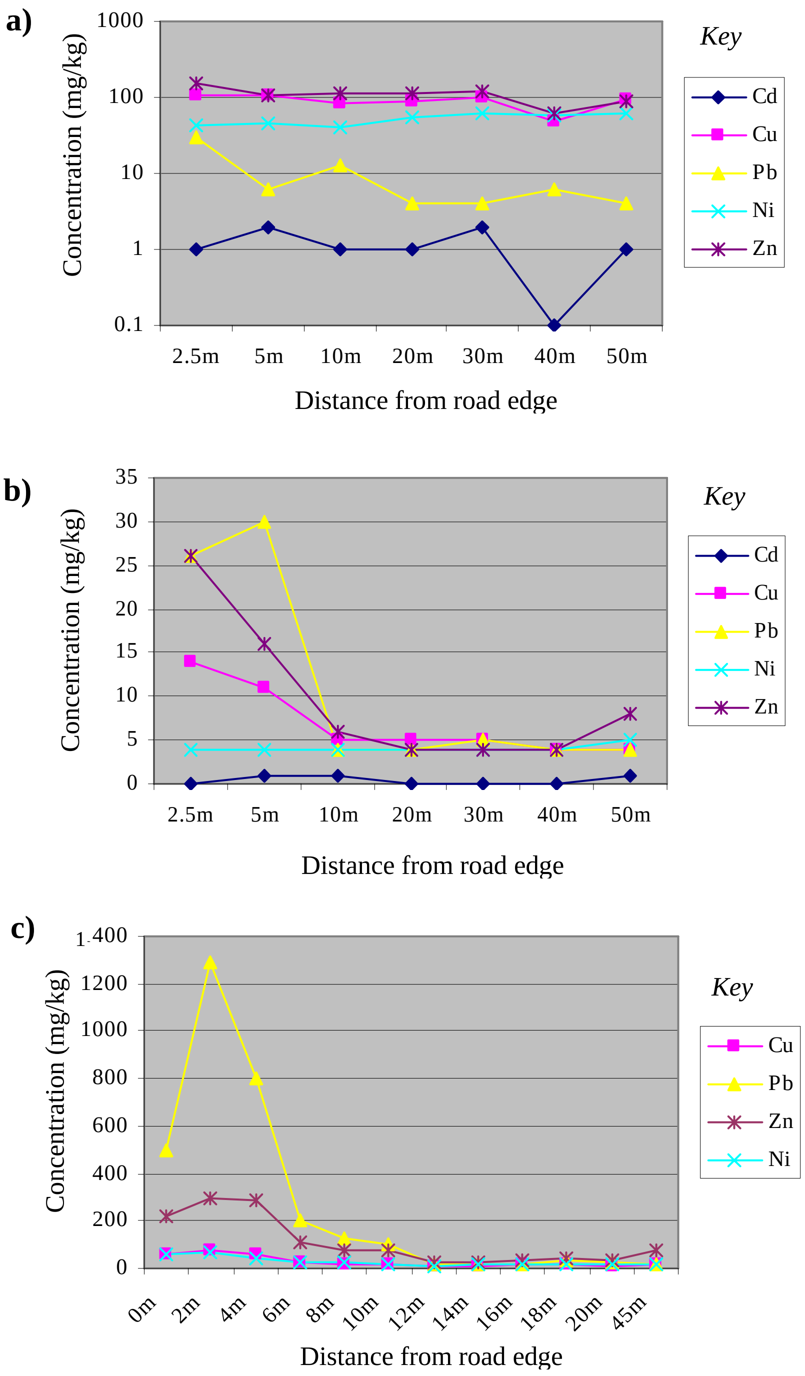

Figure 1-2: Total heavy metal concentrations in topsoils from: a) the edge of the Kuranda Range Road, upper section; b) the edge of the Kuranda Range Road, middle section (from Diprose 1999); and c) the edge of the Bruce Highway in Cairns (from Williams 2000). Note, HF-HNO3-HClO4 digestion followed by HCl leach used for total analysis in both studies.

The widely disparate results between Figure 1-2a and b may be due differences in bedrock/soil composition at the top of the Kuranda Range compared with the base. High up on the range, metamorphic base rocks may have resulted in higher soil Cu, Ni and Zn values than the sediments at the bottom of the range.

1.2.7.3 Pb isotopic ratios in topsoils adjacent to the Kuranda Range Road

Topsoil samples collected adjacent to the Kuranda Range Road by Diprose (1999) were analysed for their Pb isotopic ratios (^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb) at CSIRO in Sydney (Figure 1-3). Lead isotopes are commonly used as markers of anthropogenic-derived Pb. In any study examining Pb contamination using Pb isotopic ratios, two factors must be known, or at least reasonably assumed: a) the Pb isotopic signature of the contaminant source; and b) the Pb isotopic signature of the background material. The Pb isotopic dataset for roadside topsoils adjacent to the Kuranda Range Road compiled by Diprose (1999) lacked a distinct background Pb isotopic signature for the local soils with only one background sample analysed for Pb isotopic ratios (Figure 1-3).

Figure 1-3: ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb isotopic ratios for roadside topsoils adjacent to the Kuranda Range Road from Diprose (1999). The Broken Hill signature, growth curve and mixing lines are from Gulson et al. (1981). = background sample.

Globally, almost all Pb isotopic data for petrol additives fit in the wedge between the Broken Hill growth curve and the Broken Hill-Missouri mixing lines (Gulson et al. 1981; Chiaradia et al. 1997). Hence, the data in Figure 1-3 indicate that emissions from petrol combustion may have contributed to Pb contamination in the Kuranda Range Road topsoils. However, the significance of Diprose's (1999) Pb isotopic dataset would undoubtedly be enhanced by complementary Pb isotopic data on background substrates as well as strongly contaminated soils and sediments in the vicinity of the Kuranda Range Road.

1.2.7.4 Sediment metal values on the Kuranda Range Road

Mean heavy metal concentrations in road sediments from the Kuranda Range Road collected by Diprose (1999) were 1 mg/kg for Cd, 23 mg/kg for Cu, 39 mg/kg for Pb, 12 mg/kg for Ni, and 65 mg/kg for Zn. These concentrations do not appear to be elevated when compared with their respective values in local background topsoils. However, it must be noted that these road sediments were acquired in March and April "after a period of high rainfall" (Diprose 1999). Rainwater runoff has been documented to lower heavy metal concentrations in road sediments through dissolution (Rose et al. 2001) and by physical mobilisation of the finer-grained material which commonly hosts the greatest abundances of heavy metals (Sansalone et al. 1998; Viklander 1998). Consequently, results from Diprose's (2000) study do not represent maxima concentration data for road sediment-hosted metals in the local landscape.

1.2.7.5 Implications of previous local studies

General decrease in Cu, Pb and Zn concentrations were observed with increasing distance from road edges by both Diprose (1999) and Williams (2000). This indicates that traffic contamination was the principal source of these heavy metals in the roadside topsoils. Both of these studies revealed that the diffuse release of traffic-derived heavy metal contaminants has resulted in an imprint of elevated metal values in roadside topsoils in the Cairns area.

These reconnaissance studies warrant further investigation into the geochemistry of traffic-derived metals in roadside corridors in the Cairns region. A detailed study on the environmental fate of these contaminants is justified by these studies, with particular emphasis on metal mobility, dispersal and bioavailability in roadside environments. Such research would complement the current knowledge base on the distribution and fate of metals in roadside corridors.

1.2.8 Unexplored aspects of traffic-derived metal contamination

To date, investigations into traffic-derived metal contamination have been largely restricted to wet-temperate regions. There has been a distinct lack of research within wet-dry tropical locations. These environments are characterised by episodic flushing of road surfaces by extremely large volumes of rainfall for a few months of the year and prolonged dry periods for the remaining months.

The few studies that have been conducted in wet-dry tropical regions include the two James Cook University honours studies mentioned previously (Diprose 1999; Williams 2000). Additionally, several investigations into metal contamination in roadside soils and sediments have been carried out in Hawaii (Sutherland and Tolosa 2001; Sutherland 2000, 2002 and 2003; Sutherland et al. 2003 and 2004). These studies have researched soil/sediment total and extractable (using various acid reagents; see Table 1-4) metal contents. However, all of these investigations performed in tropical regions have been limited to assessments of metal contamination within roadside sediments and soils. They have not examined metal concentrations in road runoff waters, sediment leachates or organic tissue. Hence, the processes which affect the mobility and bioavailability of these contaminants within roadside environments in the wet-dry tropics remain unexplored.

Aside from the paucity in the number and scope of studies that have been conducted in wet-dry tropical environments, several key topics remain essentially unresearched with regards to metal contamination in roadside corridors in all types of environments. For example, specific host sites for heavy metal and PGE contaminants within road sediments and road dusts are poorly understood, with only a few studies having performed sequential extractions to infer metal hosting by road sediments (e.g. Harrison et al. 1981; Fergusson and Ryan 1984; Wang et al. 1998).

Determination of the hosting of anthropogenic metals on the surface of road sediment/dust particles is important because it represents a fundamental step in understanding the potential lability of these contaminants. The consideration of the most reactive portion of a contaminant is critical in any study where the potential negative effects of that contaminant to the environment are being assessed (Batley 2003). Recently, the advancement of analytical techniques, such as SEM coupled with EDS systems, have paved the way for detailed studies of metal/elemental associations within road sediments and dusts (Varrica et al. 2003; Rauch et al. 2004). However, there has been no emphasis placed on relating these metal/elemental associations to specific particle-type hosting of the metals. Consequently, little is known regarding the roles of various road sediment particles (e.g. tyre rubber, primary mineral fragments) in hosting anthropogenic metals.

Another aspect of roadside metal contamination that has been sparsely explored is the solubility and mobility of traffic-derived metals in road runoff waters. It has been demonstrated that metals are readily transported in both dissolved and suspended colloidal phases in road runoff waters (Bourcier 1979; Sansalone and Buchberger 1997). However, kinetic trends in aqueous metal concentrations in flowing and ponded road runoff waters are not well researched.

Furthermore, there have been no investigations that have focused on the dispersal of traffic-derived metals within streams that are intersected by roads. To date, studies that have researched anthropogenic metal contamination in stream waters and sediments have pointed to a wide array of sources in landscapes that are affected by a number of contaminating processes, including industry and mining (e.g. Lottermoser 1998; de-Vos et al. 2002). There is yet to be a single study into metal contamination within a stream system where motor vehicles and other roadside metal repositories (e.g. signposts, road paving materials) can be reasonably appointed as the principal contributing anthropogenic sources.

Additionally, while many studies have explored metal bioavailability in roadside soils, there has been no research conducted on the bioavailability of metal contaminants hosted by road sediments; with the exception of the few PGE investigations discussed in Section 1.2.5. An understanding of the bioavailability of road sediment-hosted metal contaminants is crucial, particularly in wet-dry tropical regions where metals associated with road sediments are potentially distributed over soils and into water bodies by road runoff waters. Such investigations are even more important for road corridors traversing areas containing ecosystems of national and international significance (such as the WTWHA). The contribution of sediment-hosted metal contaminants to the roadside environment is significant and cannot be overlooked.

Finally, there is considerable potential to investigate remediation options for traffic-derived metal contamination in roadside corridors. End-point and in-line tertiary remediation strategies such as lime trenches (Hamilton et al. 1999) and wetlands (Philpott 2002) that have previously been successful in the treatment of mined or heavily industrialised landscapes, are often unsuitable for roadside environments, particularly those that adjoin sensitive ecosystems. In such cases, at-source treatment is needed to mitigate the dispersal of contaminants.

1.3 Research aims and thesis outline

Only few investigations have documented the environmental fate of traffic-derived contaminants in Australia (Wylie and Bell 1973; Bottomley and Boujos 1975; David and Williams 1975; Gulson et al. 1981; Clift et al. 1983; Markus and McBratney 1996; Chiaradia et al. 1997; Birch and Scollen 2003). These studies have examined total Cd, Cu, Pb, Ni and Zn concentrations in roadside sediments, topsoils, plant tissue and airborne particulate matter. They have been conducted exclusively in subtropical and temperate locations including Melbourne, Adelaide, Sydney, Perth and Brisbane. With the exception of the two honours studies mentioned previously (Diprose 1999; Williams 2000), there are no data on heavy metal distribution in roadside sediments, soils and road runoff waters in the wet-dry tropical regions of Australia. Moreover, only one study (investigating Pd, Pt and Rh concentrations in topsoils adjacent to a major road in Perth) has examined PGE concentrations in roadside environments in Australia (Whiteley 2005).

1.3.1 Primary objective

The primary objective tackled in this project has been posed as a research question:

What are the key processes affecting the concentrations, mobility and bioavailability of traffic-derived metals in roadside environments in a section of the wet-dry tropics in northern Australia?

1.3.2 Specific aims

In order to address the primary objective, the following specific aims were formulated:

- *To determine the host sites for traffic-derived heavy metals (Cd, Cu, Pb, Ni and Zn) and PGEs (Pd and Pt) within sediments that settle on road surfaces during the prolonged 'dry season' in wet-dry tropical regions.*

- *To assess the impact of the 'first flush' road runoff waters of the 'wet season' on the solubility and mobility of heavy metals (Cd, Cu, Pb, Ni and Zn) which accumulate on road surfaces during the 'dry season'.*

- *To examine whether or not a signature of traffic-derived metal contamination can be traced into a stream system that is intersected by roads.*

- *To investigate the bioavailability of heavy metals to a grass species growing in roadside topsoils.*

- *To propose a 'treatment train' for a road upgrade in the WTWHA; including appropriate primary, secondary and tertiary remediation measures for road runoff waters.*

- *To assess the potential of common adsorptive substances (zeolite, bentonite and mushroom compost) to lower dissolved heavy metal concentrations in contaminated road runoff waters; with the objective of including the materials into tertiary remediation measures for road runoff waters.*

This research represents the first investigation into the processes by which traffic-derived metals are dispersed and sequestered within roadside environments in wet-dry tropical regions. Additionally, other novel avenues of research are pursued in this project. These include: a) an investigation into the major particle types present in road sediments and their role as host sites for traffic-derived metals; b) a study into the dispersal of metal contaminants in stream systems where roadside anthropogenic sources can be clearly identified as the principal contributors of contamination; c) an examination of the bioavailability of traffic-derived heavy metals (Cd, Cu, Pb, Ni and Zn) within road sediments that accumulate on road surfaces; and d) finally, an investigation into the kinetics of metal removal from road sediment leachates by common adsorptive materials.

1.3.3 Thesis outline

The following chapters document the PhD research. Chapter 2 outlines the general characteristics of the project area as well as the materials and methods used in the field and laboratory work conducted throughout the project. Chapter 3 examines the distributions and concentrations of traffic-derived heavy metals and PGEs in road-deposited sediments along the Kuranda Range Road and roundabouts on the urban Captain Cook Highway, Cairns. The chapter explores the geochemistry of the road sediments with particular emphasis on metal solid-phase hosting within the sediments. Also addressed in Chapter 3 are the primary factors controlling traffic-derived metal concentrations in these sediments, which include traffic density, rainfall, time, road design and physiography.

Chapter 4 examines the mobility of traffic-derived heavy metals in road runoff waters. This chapter focuses on aqueous heavy metal geochemistry through analysis of road runoff waters as well as road sediment leachate and pond samples.

Chapter 5 investigates the dispersion of traffic-derived heavy metals and PGEs in a stream system (the Avondale Creek catchment system) that is intersected by both the Kuranda Range Road and a section of the urban Captain Cook Highway. Heavy metal and PGE contamination within these stream sediments is investigated over the entire length of the creek, from its headwaters on the Kuranda Range to its major drainage estuary at one of Cairns's northern beaches. Lead isotopic ratios are used to discriminate anthropogenic Pb from natural Pb in the sediments.

The bioavailability of traffic-derived heavy metals is examined in Chapter 6. This chapter documents the uptake of heavy metals by a roadside grass species (*Melinis repens*) adjacent to the Kuranda Range Road. The measurement of heavy metal concentrations in the tissue of this grass species, and of total and DTPA-extractable heavy metal concentrations in roadside soils provides a basis on which to assess the bioavailability of these traffic-derived contaminants. The bioavailability of heavy metals hosted by road sediments is also explored through a greenhouse experiment involving the propagation of *M. repens* seeds in a substrate comprising road sediments.

Chapter 7 discusses remediation measures for the Kuranda Range Road Upgrade. An appropriate selection methodology to remediate runoff waters on the road is presented. Furthermore, the chapter assesses the effectiveness of common materials including zeolite, compost and bentonite to remove aqueous heavy metals from solution, thereby limiting their dispersal over soils and into streams in roadside environments. The chapter concludes by suggesting methods to incorporate these adsorptive materials into tertiary remediation measures for road runoff waters.

Finally, Chapter 8 summarises the main findings generated by this thesis and contains a discussion of the major limitations of the work. The chapter also provides guidance for future research in the area of traffic-derived contamination. Emphasis is placed on potential research within urban environments that encroach on pristine wilderness regions.

Each of the research chapters (3 to 7) is generally set out in the following manner: Introduction; Methods of analysis; Results; Discussion and Conclusions. Chapter 7 includes a brief technical review after the Introduction.

Chapter 2 Materials and methods

2.1 Project area characteristics

2.1.1 Project setting: environmental significance of the area

This project was conducted in a section of the WTWHA, FNQ, Australia (Figure 2-1). The WTWHA lies between the Paluma Range National Park, approximately 50 km northwest of Townsville, and the Mount Amos area, approximately 30 km south of Cooktown (Queensland Department of Main Roads 1998). The WTWHA comprises an estimated 9000 km^2 of largely continuous and protected forest, extending 400 km along the north Queensland coastline (Wet Tropics Management Authority 1999).

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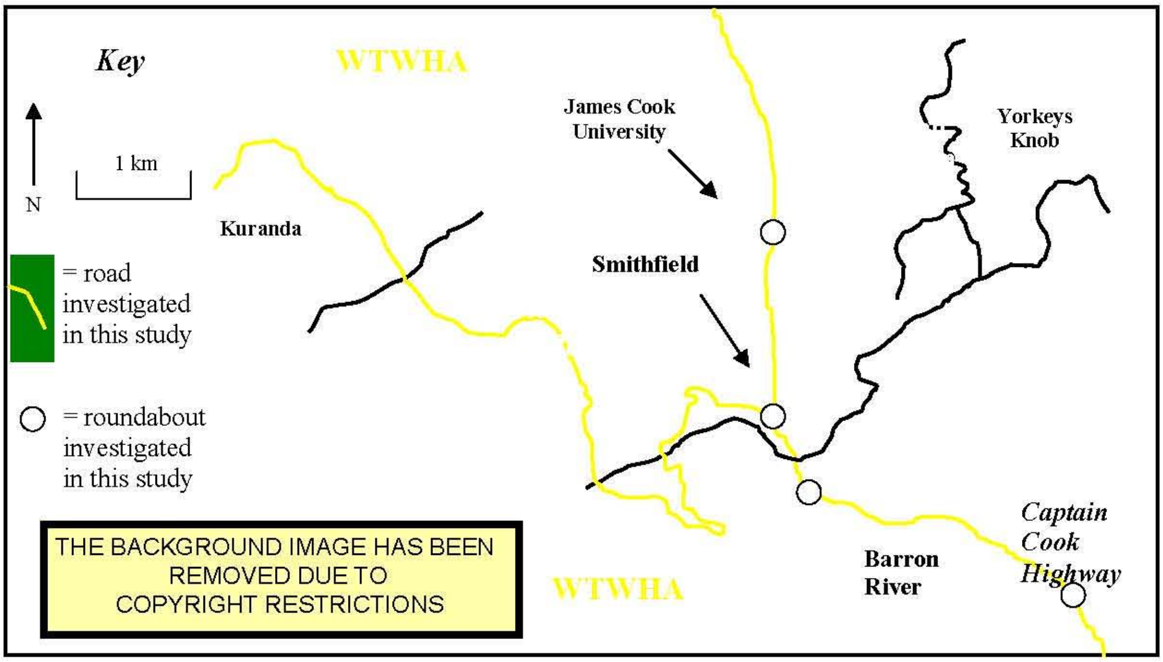
Figure 2-1: Location of the WTWHA (Bentrupperbaumer 2005).

The project is centred on the Kuranda Range Road, which intersects WTWHA-listed forest (Figure 2-2a,). Photographs of the Kuranda Range Road are presented in Figures 2-3, 2-4, 2-5, 2-6, 2-7. The road is located approximately 15 km north of Cairns. Roundabouts on the urban Captain Cook Highway, at the base of the Kuranda Range Road, were also investigated (Figures 2-2a, 2-4, 2-8).

a)



b)

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Figure 2-2: a) Aerial photograph of the project location showing major roads studied (Google Earth 2005) b) Physiography of the project area (modified from Department of Defence 1989).

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Figure 2-3: 3-D image of the proposed upgrade route of the Kuranda Range Road, indicating the steepness of the road (Searle 2004).

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Figure 2-4: Aerial photograph of the urban and rural landscape at the base of the Kuranda Range Road.

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Figure 2-5: View of the Macalister Range with the route of the Kuranda Range Road sketched in (Queensland Department of Main Roads 2004b).

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Figure 2-6: Superimposition of the Kuranda Range Road winding through WTWHA-listed rainforest (Queensland Department of Main Roads 2004b).

Figure 2-7: View of the existing Kuranda Range Road crossing with Streets Creek.

Figure 2-8: Photograph of studied roundabouts on the Captain Cook Highway.

2.1.2 Physiography

The Kuranda Range Road traverses the Macalister Range which trends north-northwest/south-southeast. The Macalister Range slopes steeply to the northeast. The major drainage system within the studied region is the Barron River which flows east into the Coral Sea. Numerous other minor stream systems also drain runoff waters from the Macalister Range into the Coral Sea (Figure 2-2b).

The Kuranda Range Road sits at a maximum elevation of 448 m above Australian Height Datum (AHD) and its lowest point is approximately 12 m above AHD (Department of Defence 1989). The Captain Cook Highway traverses low-lying plains at the base of the Macalister Range. None of the studied roundabouts are elevated more than 20 m above AHD (Department of Defence 1989).

2.1.3 Climate

The project area is situated in the wet tropics region of Queensland; a location that is characterised by distinct wet and dry seasons. Average annual rainfall in the project area is reported to be between 1800 and 2400 mm (BOM 2004), although annual rainfall values in excess of 8000 mm for specific areas within the Cairns region have been documented (Goosem and Tucker 1995). The highest rainfall in the wet tropics region is generally recorded between December and April (Figure 2-9). Over this period, approximately 75 to 90 % of the annual rainfall occurs (Queensland Department of Main Roads 1998). From the months of June to October, the average monthly rainfall in the region is below 50 mm (BOM 2005b).

Maximum daily temperatures are recorded in December and January in the Cairns area (Figure 2-10). The average maximum daily temperature in both December and January is 31.5 ^{o}C (BOM 2005c). Minimum daily temperatures are generally recorded in July (17.5 ^{o}C) in the Cairns region (Figure 2-10) (BOM 2005c).

Cairns and surrounding regions are subject to tropical cyclone activity (Queensland Government 2005). On average, Cairns and its neighbouring suburbs experience one cyclone every two years, although direct hits by severe cyclones on the city of Cairns are uncommon (Queensland Government 2005).

Figure 2-9: Average monthly rainfall for the Cairns area (BOM 2005b).

Figure 2-10: Average maximum and minimum monthly temperatures for the Cairns area (BOM 2005c).

2.1.4 Geology

The local geology, in addition to climate, in the Cairns-Kuranda region controls the natural metal content of soils and sediments in the project area. The outcropping rock units encountered in the project area are predominantly ascribed to the Hodgkinson Formation (Figure 2-11). The Hodgkinson Formation comprises Silurian/Devonian successions of siliciclastic arenite and mudstone, with minor conglomerate, chert, sparse basalt and limestone deposited in a marine environment (Bain and Draper 1997).

A Carboniferous granitic intrusion mapped as part of the Mount Formartine Granite occurs on the upper section of the Kuranda Range Road (Figure 2-11). According to Bain and Draper (1997), the Mount Formartine Granite is characterised by a low Pb content relative to other similar granitic bodies in the Hodgkinson Province, although no specific values are presented. Quaternary alluvial and beach dune sediments are common on the plains through which the urban Captain Cook Highway traverses (Bain and Draper 1997).

Figure 2-11: Local geology of the project area (modified from Bain and Draper 1997).

2.1.5 Geomorphology

The development of a number of gorges within the Macalister Range has resulted in the continuous supply of sediments from higher altitudes to form alluvial fans, slope deposits and coastal sedimentary landforms (Nott 2003). Based on work by Nott (2003), the area investigated in this project may be crudely separated into four types of terrain (Figure 2-12). The Macalister Range is characterised by steep escarpments; the base of the range accommodates alluvial fans; the landscape beyond the foot of the range is dominated by sediment-filled flood plains; and the coastal terrain largely comprises dune systems that are incised by delta fans (Nott 2003).

The presence of debris flows documented in several of the alluvial fan systems in the Cairns area suggests that there have been a number of extensive landslides within the region (Nott 2003). Large-scale debris flows, dated as Pleistocene age, have been recorded at the base of the Macalister Range (Nott 2003). Smaller-scale Holocene debris flows have been recorded overprinting these Pleistocene formations (Nott 2003).

Currently, the region continues to experience continual landslides as a result of natural geomorphologic and climatic conditions as well human activities (such as land clearing) (Nott 2003). However, magnitudes of current landslides are much lower than those that occurred during the Pleistocene (Nott 2003).

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Figure 2-12: Geomorphology of the project area (modified from Nott 2003)

2.1.6 Soils

The uptake of heavy metals by vegetation growing in roadside soils is a major avenue of research pursued in this study. Consequently, it is important to establish background soil-metal levels in the area and to determine various parameters of these soils which are good indicators of the soil's ability to retain metals (e.g. soil pH and C_{org} levels).

The soils encountered in the project area can be broadly segregated into three main types, according to Murtha et al. (1996). Soil series intersected by the Kuranda Range Road include the Bicton, Bingil, Buchan, Galmara and Mission Series (Figure 2-13). These soils have been mapped as having been developed from a metamorphic rock substrate (Murtha et al. 1996).

The section of the Captain Cook Highway investigated in this project traverses soils ascribed to the Buchan, Clifton, Holloway, Liverpool and Mission Series (Figure 2-13). These soils have metamorphic and alluvial origins (Murtha et al. 1996). Soils in the low-lying terrain to the east of the Captain Cook Highway are ascribed to the Liverpool Series (formed on well-drained alluvium); the Brosnan, Googarra, Hull and Spanos Series (formed on beach ridges); and two series mapped as Mangrove Systems and Made Land (Murtha et al. 1996).

Figure 2-13: Soil series encountered in the project area (modified from Murtha et al. 1996).

Soil properties shown in Table 2-1 indicate that the soils on the Macalister Range generally display lower pH values and contain slightly higher C_{org} values than the soils adjacent to the roundabouts on the Captain Cook Highway. CEC values for the soils do not show much variation between those metamorphic rock-derived soils adjoining the Kuranda Range Road and the alluvial soils adjacent to the Captain Cook Highway roundabouts (Table 2-1).

While there are no records of heavy metal contents in topsoils in the project area, Cu and Zn concentrations have been recorded in several soil series mapped by the CSIRO Division for Soils approximately 10 km south of the project area (Murtha et al. 1996). These soils are derived primarily from weathered granite rather than weathered metamorphic bedrock. In the Prior, Kirrama, Canoe, Jarra, Virgil, Timara and Malbon Series, a range of Cu concentrations (<5 mg/kg to 58 mg/kg) and Zn values (20 mg/kg to 98 mg/kg) have been found (Murtha et al. 1996).

Table 2-1: Properties of topsoils (to 10 cm bgs) in soil series encountered in the project area (from Murtha et al. 1996). * *Sum of acidic and basic ions.*

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2.1.7 Vegetation

The wet tropics region in Far North Queensland contains the greatest diversity of plant families and genera in Australia (Queensland Department of Main Roads 1998). Forty-three plant genera are entirely restricted to the wet tropics region (Queensland Department of Main Roads 1998). Medium to low woodland, characterised by species of Eucalyptus, Lophostemon, Melaleuca and Acacia, is the dominant vegetation type described for the area at the base of the Kuranda Range Road (Tracey and Webb 1975). Further up the range, pockets of notophyll vine rainforest are present and at the top of the range closed mesophyll vine forest and vine forest with some stands of sclerophyll emergents such as acacias are predominant (Tracey and Webb 1975). The principal vegetation type in the vicinity of the urban Captain Cook Highway consists of planted grasses and crops, predominantly sugar cane (Tracey and Webb 1975).

The immediate edge environment adjacent to both the Kuranda Range Road and the Captain Cook Highway roundabouts, like most clearings in tropical regions, hosts significant weed populations. Grass species, including Guinea grass (*Panicum maximum*), dominate the road edge on the upper section of the Kuranda Range Road where canopy cover is dense and light penetration in minimal. However, along the lower and more open section of the Kuranda Range Road, and on the roundabouts on the Captain Cook Highway, grass species including Red Natal grass (*Melinis repens*) and Rhodes grass (*Chloris gayana*) dominate the road edge environment.

2.1.8 Road properties and traffic volumes

The Kuranda Range Road was constructed in 1940 (Cherry 2005). The road is composed of bitumen/asphalt with concrete gutters present along certain sections of the road (Figure 2-14). For the remainder of the road's edge, the bitumen surface is in direct contact with the surrounding natural ground surface.

Diprose (1999) states that there are a total of 100 bends on the road, although it would seem extremely difficult to accurately summarise this particular aspect of the road. The course of the road is extremely convolute. Some statistics for the Kuranda Range Road are presented in Table 2-2.

Table 2-2: Various statistics for the Kuranda Range Road (Cherry 2005)

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The Queensland Department of Main Roads intends to upgrade the existing Kuranda Range Road from two lanes to four (Queensland Department of Main Roads 2004c). The proposed timeframe for the upgrade completion is 10 years. However, no specific commencement date has been indicated for the works (Queensland Department of Main Roads 2004e).

The Captain Cook Highway roundabouts studied in this project were constructed between 1987 (Machans Beach Roundabout) and 1993 (McGregor Road Roundabout) (Jones 2004). The road surface on these roundabouts is bitumen (Figure 2-15). Road runoff waters are channelled along concrete gutters on the inside of the roundabouts through regularly-spaced drainage gaps. The centre of each of the studied roundabouts consists of depressed grassed embankments. The roundabouts on the Captain Cook Highway have an average traffic density of 30,000 vehicles per day (Jones 2004).

Figure 2-14: Photograph of the road surface of the Kuranda Range Road, along with a concrete drainage structure.

Figure 2-15: Photograph of the surface of the Captain Cook Highway roundabouts. A drainage structure common to the roundabouts is shown in the centre of the image.

2.1.9 Land uses within the project area

The Kuranda Range Road intersects National and State Forest Park-listed land (Figure 2-16). The Skyrail cableway, which passes over the Kuranda Range Road at two locations (Figure 2-16), is a tourist facility consisting of suspended cable-cars. It is run on electricity and does not generate any exhaust emissions. It is possible, but not established, that the facility releases minor amounts of metals into the underlying rainforest as a result of mechanical abrasion.

The section of the Captain Cook Highway investigated in this study passes through sugarcane farms and commercial retail outlets (Figure 2-16). There is a clear absence of heavy industry within the project area. Thus, activities that potentially contribute to the release of anthropogenic metal contaminants within the project area include: a) vehicular traffic, road infrastructure and paving materials; b) operations of the Smithfield Sewage Treatment Plant; and c) the application of fertilisers to sugarcane farms.

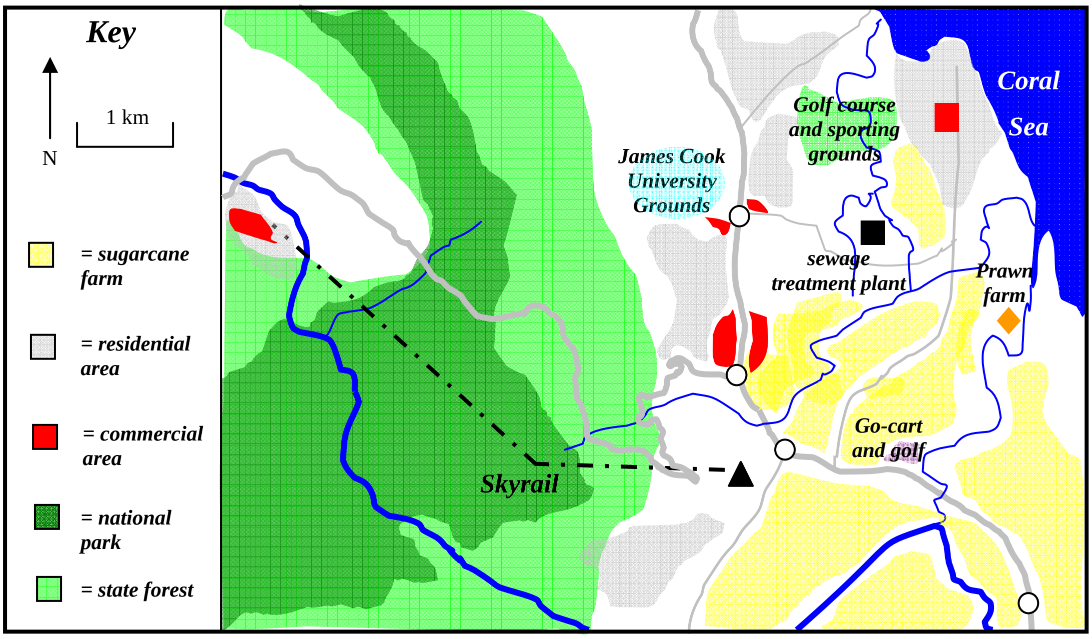


Figure 2-16: Major land uses within the project area.

2.2 Sample collection and labelling

A number of field and laboratory samples were collected and analysed over the course of this project. Field samples are denoted by a letter representing their sample location (e.g. C = Captain Cook Highway), a subsequent letter indicating the sample type (e.g. R = road sediment) and finally the sample number. By comparison, all samples collected from laboratory experiments in the project are signified by the letter ‘L’ and their respective number. Composite and sieved fraction road sediment samples are denoted by further characters (C_M for composite samples and R_F for sieved fraction samples). Table 2-3 indicates the meaning of the various sample ID characters used throughout the thesis. In addition, a few examples of sample ID labels are presented in Figure 2-17. Complete sample ID details, including AMG coordinates and sample descriptions, are presented in Appendix A.

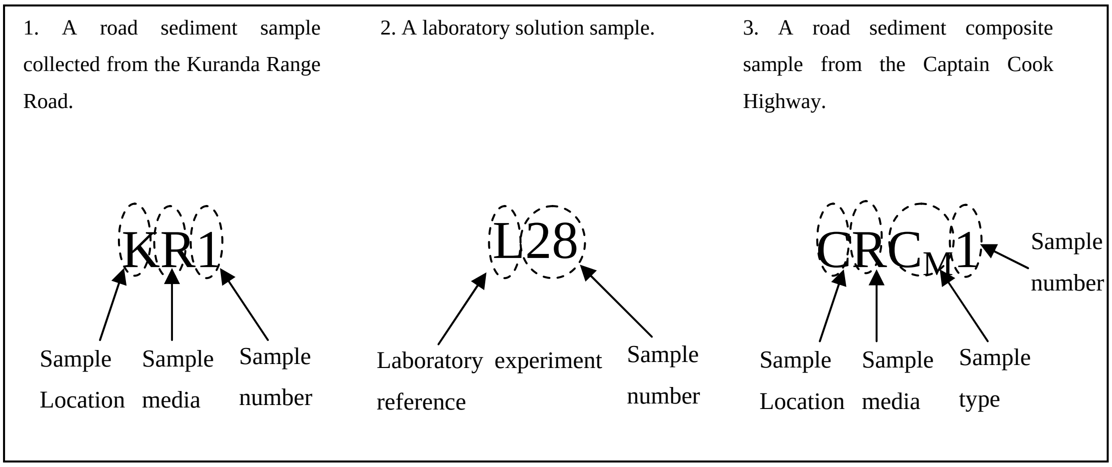


Figure 2-17: Examples of sample ID used in this thesis.

Table 2-3: Descriptors for sample ID used in this thesis.

Location character	Sample media character	Sample type character
K = Kuranda Range Road	B = bedrock sample	C_M = composite road sediment sample
C = Captain Cook Highway	R = road sediment	R_F = sieve fraction of road sediment sample
D = Davies Creek area	S = stream sediment	
	W = road runoff waters	
	S_W = stream water sample	
	R_W = rainwater sample	
	T = topsoil sample	
	G = grass sample	

2.3 Bedrock samples

2.3.1 Rationale

Bedrock samples were collected to determine the influence of parent rock geochemistry on soil and sediment metal concentrations within the project area. The three major rock types encountered in the study area were sampled: a) granite from the exposed section of the Mount Formartine Granite; b) hornfels from the contact zone with the granite body; and c) metasiltstone from the Hodgkinson Formation (Figure 2-11).

2.3.2 Collection methods

Samples were obtained from each rock type using an Eastwing geopick, with care taken not to collect weathered surfaces. Five separate samples of approximately 200 g were collected from each of the three major rock types (so that there were a total of 15 individual samples). AMG coordinates for the bedrock sample locations are presented in Appendix A.

2.3.3 Sample processing

The individual samples were crushed to powder in a chrome steel ring mill. Each of the samples was then combined to produce a single representative sample for each of the three major rock types, so that there were a total of three representative bedrock samples. Bedrock samples are denoted by the prefix ‘B’ (Appendix A). Sample B1 is a representative sample of the granite outcrop; B2 was compiled from the metasiltstone samples; and B3 was produced by samples taken from the Hornfels contact with the granite.

2.3.4 Chemical analyses

The three bedrock samples (B1, B2 and B3) were analysed for total Cd, Cu, Pb and Ni values by ICP-MS and total Zn levels by ICP-AES following digestion in HF-HNO_3-$HClO_4$ and for Pd and Pt by ICP-MS following fire assay. The samples were analysed at ALS, Brisbane.

2.4 Road and stream sediments

2.4.1 Sampling

Road sediment samples were swept from road edges (Figures 2-19 and 2-20) into a dustpan, taking care not to unsettle the fine dust component. Disturbance of this fine portion of road sediments may result in its loss to the atmosphere (Serrano-Belles and Leharne 1997). Samples were stored in paper bags. The road sediments were obtained in October 2002, November 2003 and August 2004. Sediment samples were also collected from the Kuranda Range Road in August 2003 to supplement the dataset. Sampling was conducted following extended dry periods in order to obtain sufficient material that was unaffected by surface water runoff and associated leaching processes.

Road sediments were acquired from nine locations on the Kuranda Range Road and from four locations on the Captain Cook Highway roundabouts (Figure 2-18). Over the duration of the study, a total of thirty sediment samples were taken from the Kuranda Range Road, while eleven sediment samples were collected from the Captain Cook Highway roundabouts. Additionally, three road sediment samples were obtained from a straight section of the Captain Cook Highway in October 2002 (CR5-CR7, Figure 2-18).

Stream sediments were taken from the headwaters of Streets Creek at the top of the Macalister Range and Avondale Creek, which is intersected by both the Kuranda Range Road and the Captain Cook Highway (as well as smaller connecting roads) (Figure 2-18). These wet sediments were acquired from the top 5 cm of the active stream channel bed with a plastic scoop and stored in plastic zip-lock bags. The stream sediments from Streets Creek were sampled in February 2004, while the stream sediments from Avondale Creek were collected in October 2004. A total of eight stream sediment samples were taken from Streets Creek, while seventeen samples were taken from Avondale Creek.

Approximately 500 g of sediment was collected from each location, for both the road and stream sediment samples. The road sediments were retained in their paper bags while the saturated stream sediments were transferred to borosilicate glass beakers upon return to the laboratory. Sediment sample details, including AMG coordinates, are presented in Appendix A.

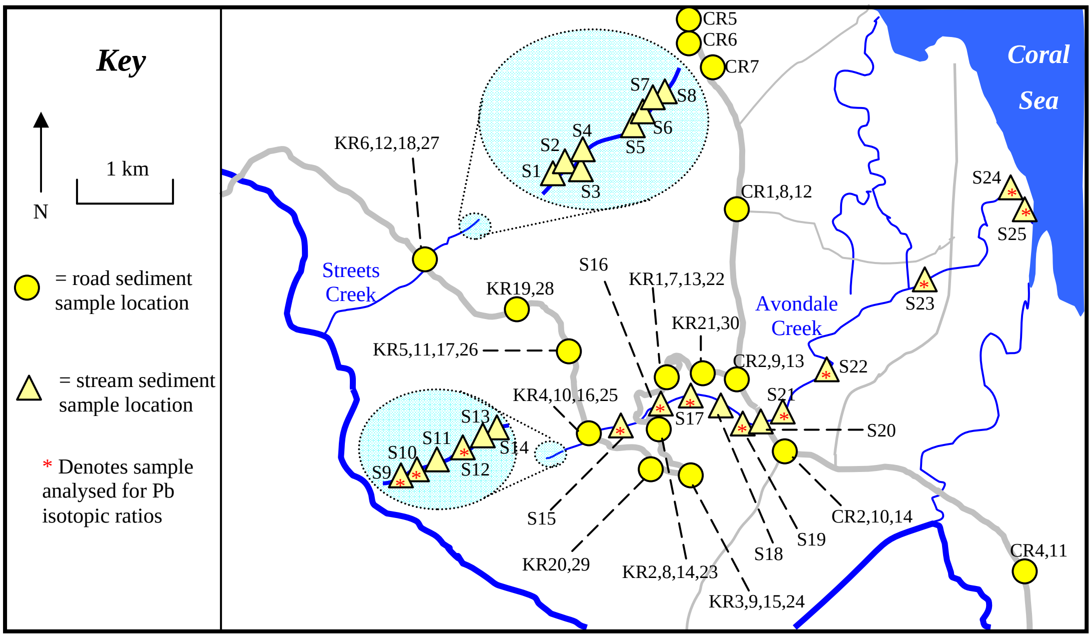


Figure 2-18: Road sediment and background stream sediment sample location plan (AMG coordinates are given in Appendix A).

2.4.2 Sample processing

All sediments were oven-dried at 50°C (Sures et al. 2001). The samples were mixed thoroughly on an individual basis to ensure homogeneity. A small proportion (approximately 50 grams) of road sediment collected from each location over the various sampling periods was sieved to less than 2 mm to remove coarse rock fragments and organic debris (Sures et al. 2001). The same was done for all stream sediment samples from Streets Creek and the background samples (i.e. those upstream of roads) from Avondale Creek (i.e. S9 to S14, Appendix A). Sediments were crushed in a chrome steel ring mill to powder.

Figure 2-19: Gutter from which road sediment samples KR21 and KR30 were collected, Kuranda Range Road. Refer to Appendix A for sample ID details.

Figure 2-20: Gutter on roundabout on the Captain Cook Highway from which road sediment samples CR1, CR8 and CR12 were acquired. Refer to Appendix A for sample ID details.

2.4.3 Sieving

2.4.3.1 Road sediments

A homogeneous composite sample (KRC_M1, Appendix A) was produced comprising equal portions of individual road sediment samples KR1 to KR6. The bulk sample was placed into a stack of brass sieves (aperture intervals were: <38 µm, 38 µm - 63 µm, 63 µm -75 µm, 75 µm -106 µm, 106 µm – 250 µm, 250 µm – 500 µm, 500 µm - 1000 µm, 1000 µm – 2000 µm, 2000 µm – 4000 µm and >4000 µm). The same procedure was performed on another composite sample, CRC_M1 (Appendix A) made from aliquots of individual samples CR1 to CR4 (Appendix A).

For the purposes of replication, sieving was again carried out on two bulk sediment samples labelled KRC_M2 and CRC_M2 (Appendix A). These composite samples consisted of portions of individual samples KR13 to KR21 and CR8 to CR11, respectively, which were acquired in November 2003 (Appendix A). Fewer sieve intervals were used for the November 2003 bulk samples, and these were deemed adequate to effectively characterise the grain size distribution (aperture intervals were: <38 µm, 63 µm – 75 µm, 106 µm – 250 µm, 500 µm - 1000 µm and 2000 µm – 4000 µm).

Further grain size distribution patterns were determined for two composite road sediment samples, taken from the Kuranda Range Road (KRC_M3 comprising KR22 to KR30, Appendix A) and the Captain Cook Highway roundabouts (CRC_M3 consisting of CR12 to CR14, Appendix A), respectively in August 2004. These samples were sieved to 2000 µm – 250 µm, 250 µm – 75 µm, 75 µm – 38 µm and <38 µm. For all sieved samples, the sediment weight in each sieve interval was measured. A portion of sediment in each interval was crushed in a chrome steel ring mill to powder in readiness for chemical analyses.

2.4.3.2 Stream sediments

Three stream sediments collected from the Avondale Creek catchment (S9, from upstream of all roads; S21, from downstream of the Kuranda Range Road but upstream of the Captain Cook Highway; and S25, from the estuary mouth of the catchment system, Appendix A) were separated into the clay and silt fraction (<75 μm grain size) by dry sieving through a brass sieve.

Sieving of these sediments into various grain size intervals within this fraction was carried out using a Malvern Mastersizer Laser Particle Size Analyser (JCU, Townsville). This instrument is able to identify solid grains down to 0.1 μm in diameter.

2.4.4 Mineralogical analyses and SEM observations

Twenty grams of composite road sediment samples KRC_M1 and CRC_M1 (Appendix A) were crushed to powder in a chrome steel ring mill and a portion of each sample was analysed using a Siemens D5000 X-ray difractometer equipped with a theta-2 theta goniometer at the AAC, Cairns. The mineralogy of the samples was determined by using the EVA software computer package in tandem with the XRD system.

Portions of KRC_M1 and CRC_M1 were also viewed under optical microscopy to observe their general composition. Additionally, small aliquots of both of these composite sediment samples were placed on metallic stubs and spray-coated with carbon to be analysed under a JEOL JSM – 6300 SEM equipped with an EDS system (AAC, Cairns).

2.4.5 Extraction techniques

2.4.5.1 Sequential extraction

A sequential extraction was performed on bulk road sediment sample, KRC_M3 (Appendix A) in order to separate metals associated with 6 different fractions: water-soluble; exchangeable; carbonate; Fe-Mn oxides/oxyhydroxide; organic/sulphide; and residual silicate. The extraction was conducted in the earth sciences wet laboratory at James Cook University, Cairns Campus. Analytical grade chemicals supplied by Selby Biolab Australia were used in the extractions. The extraction followed the method given by Tessier et al. (1979) with one major exception. Five individual sample aliquots of road sediment were used, with one aliquot used in each step of the extraction sequence, rather than using one portion of sediment throughout the entire sequence. This modification was implemented to overcome the problem of sample loss between steps in sequential extraction procedures, which has been well-documented in the literature (Tessier et al. 1979). The specific steps used in the extraction sequence are detailed in Appendix C. An account of how the results of the sequential extraction were evaluated is also included in Appendix C.

Approximately 20 g of the bulk sediment sample KRC_M3 was sieved to less than 250 µm, in accordance with the method given by Tessier et al. (1979). One gram of sediment was placed into six separate glass test tubes. Following the completion of each step in the extraction procedure, the solutions were centrifuged at 4000 rpm for 20 minutes to obtain clear extracts. The extracts were analysed at the AAC, Townsville and details of their chemical analyses are presented in Section 2.4.7.2.

Determination of the total heavy metal content of the road sediment used in the sequential extraction was necessary, to calculate the proportion of metals that released from the road sediments into the extraction solutions. Thus, three sediment subsamples (sieved to less than 250 µm) of KRC_M3 were crushed to powder in a chrome steel ring mill. The powdered samples were analysed at ALS, Brisbane and Section 2.4.7.1 provides information regarding their analyses for total metal contents.

2.4.5.2 Citrate-dithionite extraction

Aliquots of bulk road sediment samples KRC_M3 and CRC_M3 were used for this partial extraction, which targets the Fe-Mn oxide/oxyhydroxide fraction. The two bulk sediment samples were sieved to less than 0.5 mm, in accordance with

Rayment and Higginson (1992). Four aliquots of each of the two bulk sediment samples were weighed out separately into 250 mL polyethylene plastic bottles (so that there were a total of 8 bottles with sediment).

A solution of 22 % Na-citrate solution was prepared following the procedure by Rayment and Higginson (1992) (Appendix C). Fifty millilitres of this solution and 1 g of Na-dithionite were added to each bottle. The test tubes were capped and mechanically shaken end-over-end for 16 hours. The solution from each bottle was poured into a plastic screw-cap test tube. Each tube was centrifuged for 20 minutes at 4000 rpm and then left loosely capped for 2 days. The extracts were retained and sent to the AAC, Townsville for analyses. The details of the chemical analyses are outlined in Section 2.4.7.2.

To determine the proportion of metals released from the road sediments into the extraction solutions, the total heavy metal content of the road sediment used in the citrate-dithionite extractions was established. Hence, portions of KRC_M3 and CRC_M3 (sieved to less than <500 μm) were crushed to powder in a chrome steel ring mill. The powdered samples were submitted to ALS, Brisbane and analysed for their total metal contents. Section 2.4.7.1 discusses details of the analyses.

2.4.5.3 DTPA and EDTA extractions

The amounts of DTPA-extractable and EDTA-extractable heavy metals in the road sediments collected from the Kuranda Range Road and the Captain Cook Highway roundabouts in August 2004 were determined by using the methods described by Rayment and Higginson (1992). This was done to evaluate the bioavailable proportion of metals in the road sediments. One variation to the method (Rayment and Higginson 1992) included the use of 2.5 g of sediment rather than the prescribed 25 g (the sediment solution ratio remained 1:2). Precision of the results was evaluated by processing four aliquots of the same sample from the Kuranda Range Road and the Captain Cook Highway roundabouts.

Portions of composite sediment samples KRC_M3 and CRC_M3 were used in this experiment. Four aliquots of the Kuranda Range Road bulk road sediment sample and four aliquots of the Captain Cook Highway roundabouts bulk sediment sample were sieved to less than 2 mm and crushed to powder (Rayment and Higginson 1992).

The DTPA and EDTA extracts were analysed at the AAC, Townsville, whereas the powdered solid samples were examined at ALS, Brisbane. Sections 2.4.7.1 and 2.4.7.2 outline the analytical procedures for the determination of the total and DTPA and EDTA extractable heavy metal contents of these samples, respectively.

2.4.6 Laboratory experiments

2.4.6.1 Column leach experiments

All equipment used in the experiments was rinsed with 0.1 M HCl and distilled water. Two bulk road sediment samples, KRC_M1 and CRC_M1, were subject of a column-leach experiment. One-hundred grams of each composite sample were placed into a clear plastic column. The sediment was mixed with quartz gravel and sand to increase its permeability (see Figure 2-21). Two-hundred millilitres of distilled water were poured into each column. The distilled water used in this study had a pH of approximately 5.7 due to the formation of carbonic acid upon equilibration of the water with the atmosphere. This pH value is very similar to that of pure rainwater (Fifield and Haines 1995). Nine further 200 mL volumes of distilled water were poured through each column, so that a total of ten leachate samples were collected for each bulk sediment over the duration of the experiment. A total of 2 L was leached through each column, and the reaction time of each leach volume with the sediment was recorded. The pH, DO and Eh in each leachate sample were recorded using a Radiometer Analytical pH/Eh210 instrument for pH and EH and a Hanna oxygen probe.

Determination of the total heavy metal content of the road sediment used in the column leach experiment was necessary so that metal values in the leachates could be related back to the total sediment values. Thus, three replicate sediment subsamples of KRC_M1 and CRC_M1 were crushed to powder in a chrome steel ring mill. Analyses of the metal content of these replicate samples are discussed in Section 2.4.7.1.

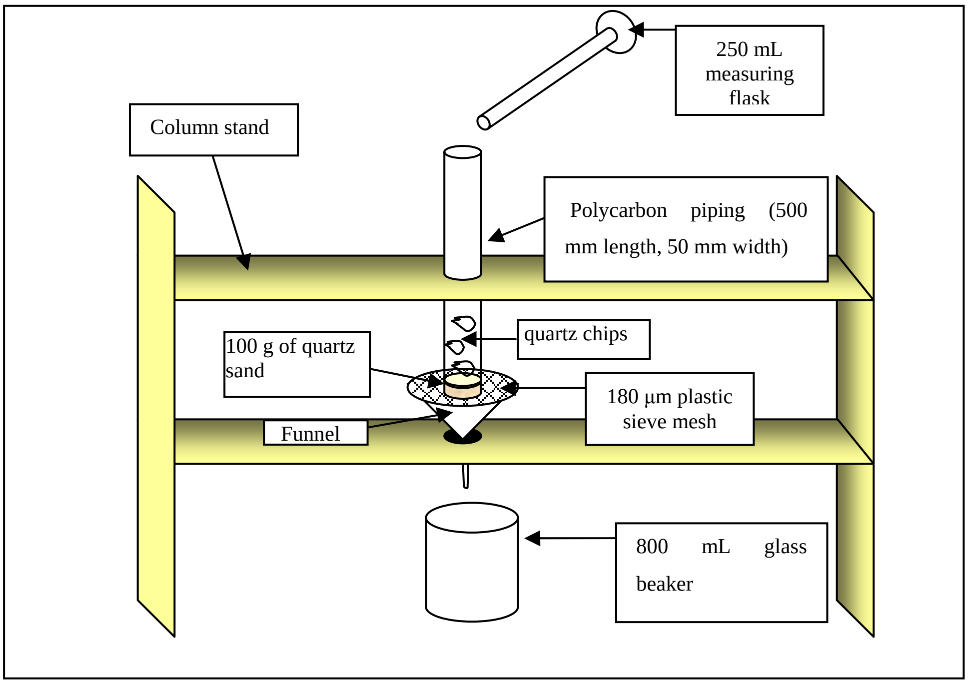


Figure 2-21: Set-up of the column stand for the column leach experiments.

2.4.6.2 Ponding experiments

All equipment used in the experiments was rinsed with 0.1 M HCl and distilled water. One-hundred grams of sample KRC_M1 was placed into an 800 mL glass beaker. A section of plastic mesh with sieve apertures of 180 µm was placed over the sediments in the beaker and a handful of quartz gravel was placed on the mesh to weigh it down. Two-hundred millilitres of distilled water was poured into the beaker and allowed to settle for 5 minutes. The pond water was then decanted from the beaker using a pipette, with care taken not to disturb the sediment. Further 200 mL volumes of distilled water were ponded with the sediments and then decanted after 1 hour, 24 hours, 1 week and 1 month, respectively. The beaker was covered with paraffin wax to prevent evaporation. The pH, DO and Eh in each leachate sample were recorded using a Radiometer Analytical pH/Eh210 instrument for pH and EH and a Hanna oxygen probe.

The same experiment was performed on bulk sample CRC_M1. However, this experiment was conducted over a longer period of time, so that a total of eight pond decant samples were collected. Samples were taken after: 5 minutes; 1 hour; 24 hours; 48 hours; 1 week; 5 weeks; 6 weeks; and 3 months.

2.4.6.3 Preparation of the column leachates and pond decant samples

Column leachate and pond decant samples were split into two sub-samples; one was filtered through 0.45 µm Millipore filter paper (supplied by Selby Biolab) and poured into a polyethylene plastic bottle, the other was poured without being filtered into a polyethylene bottle. Samples were acidified to pH <2 with two drops of 70 % HNO_3 and sent to the AAC, Townsville for analyses. The chemical analyses of the leachate and pond extracts are detailed in Section 2.4.7.2.

2.4.7 Chemical analyses

2.4.7.1 Solid samples

All individual road and stream sediment samples whose locations are indicated on Figure 2-18 were analysed for their Cd, Cu, Pb, Ni and Zn contents. A number of these samples were also analysed for their Pd and Pt concentrations (listed in Appendix A and B). The various size fractions of the dry sieved road sediments were examined for their total Cd, Cu, Pb, Ni, Zn as well as Pd and Pt values (Appendix A, B). Furthermore, the replicate subsamples of the composite road sediment batches used in the leaching techniques and laboratory experiments were examined for their Cd, Cu, Pb, Ni and Zn concentrations (Appendix A, B). Cadmium, Cu, Pb and Ni levels were determined by ICP-MS and Zn concentrations were measured by ICP-AES following sample digestion in $HF-HNO_3-HClO_4$. Palladium and Pt concentrations were determined by ICP-MS following fire assay. All samples were analysed at ALS, Brisbane. In addition, the road sediment samples (sieved to <2 mm) collected in October 2002 (KR1-6 and CR1-7, Appendix A) were analysed for their Al, Fe and Mn contents by a Bruker – AXS S4 Pioneer X-ray fluorescence spectrometer at the AAC, Townsville.

Representative road sediment samples, one from the Kuranda Range Road (KR13, Appendix A) and one from the Captain Cook Highway roundabouts (CR9, Appendix A), were examined for total carbon by measurement of CO_2 gas in a NDIR gas analyser following combustion in a LECO furnace at 950 ^{o}C. Inorganic carbon was determined by measurement of CO_2 gas in a NDIR gas analyser following digestion of the sample in HNO_3 and heating to 250^{o}C in the LECO furnace. Organic carbon levels in these samples were determined by subtracting the inorganic carbon values from the total organic carbon values. Carbon analyses were performed at ALS, Brisbane.

Three of the stream sediments (<75 μm fraction) collected from the Avondale Creek catchment system (S9, S21 and S25 - Appendix A) were also assessed for their Al, Fe and Mn contents as well as for their organic and inorganic carbon contents at the AAC and ALS, respectively. The $S_{sulfate}$ and $S_{sulfide}$ contents of these samples were also examined. $S_{sulfate}$ levels were measured gravimetrically by precipitation of $BaSO_4$ following leaching of the sediments with weak HCl. Total sulfate was measured gravimetrically by precipitation of $BaSO_4$ following leaching of the sediments with strong HNO_3 and Br (this converts all reduced S to SO_4^{2-}) and weak HCl. $S_{sulfide}$ levels were determined by subtracting the sulfate S values from the total S values. All sulfur analyses were performed at ALS, Brisbane. Data for all sediment samples analysed in this project are given in Appendix B.

2.4.7.2 Laboratory leachates, pond decant samples and extracts

Cadmium, Cu, Pb, Ni and Zn concentrations were determined by ICP-MS in all laboratory leachates, pond decant samples and extracts. Aluminium, Ca and Fe concentrations were measured by ICP-AES in the column leachate and pond decant samples. All samples were analysed at the AAC, Townsville. Analytical data for these samples are presented in Appendix B.

2.4.8 Pb isotope analyses

Three road sediments (Appendix A) and twelve stream sediments taken from the Avondale Creek catchment system were prepared for Pb isotopic analysis (sample locations are given in Figure 2-18 and location coordinates are listed in Appendix A). The sediments were all sieved to <75 μm in order to produce uniform sediment samples, which otherwise displayed variable proportions of coarser, eroded rock material. Samples were analysed for their Pb isotopic ratios (^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios) at CDU, Darwin. To supplement the Pb isotope database, portions of the same twelve stream sediment samples that were sent to CDU were also analysed at ANSTO, Sydney, along with three other road sediment samples (Appendix A). Determination of the ratios of the less common ^{204}Pb isotope to the previously mentioned isotopes (^{208}Pb, ^{207}Pb and ^{206}Pb) was included in the analysis conducted at ANSTO.

Lead isotope analysis was performed by quadropole ICP-MS at both CDU and ANSTO (instrument type: Aligent 4500 for ANSTO; ELAN 6000 for CDU). At CDU, isotopes were analysed following digestion of the sediments in HNO_3-$HClO_4$. While this digestion technique is unable to result in the total dissolution of some silicates (e.g. quartz, feldspars and zircon) Munksgaard (pers. com. 2004) notes that "*in chemically and physically mature sediments, as predominantly found along the north Australian coastline, the vast majority of metals are associated with clays and Fe-oxy-hydroxides along with organic matter and sulfides. In such sediments, digestion by perchloric and nitric acids are vigorous enough to allow pseudo-total analysis of most heavy metals*" (Munksgaard 2004).

At ANSTO, isotopes were analysed following digestion of the sediments in HF-HNO_3-HCl. This digestion technique is stronger than that provided by CDU, given the aggressiveness of the HF reagent.

2.5 Road runoff, rainwater and stream waters

2.5.1 Sampling

Road runoff water samples were collected from locations indicated in Figure 2-22. The AMG coordinates of these sample locations are presented in Appendix A. The samples were collected during the 'wet season' in February 2003 and January 2004 and prior to the 'wet season' in November 2004.

Samples were collected in HCl-rinsed 250 mL polyethylene bottles (supplied by ALS), which were modified to include a floating stop (ping-pong ball). The floating stopper was necessary to ensure that the 'first flush' waters of the documented rainfall events were captured. Without this stop device the road runoff water samples in the bottles would have become progressively diluted (Han et al. 2005). Bottles were left in the field in order to sample the earliest stages of the rainfall events. The bottles were left for a maximum of 2 days in the field, after which time bottles were replaced by fresh ones to avoid the problem of dust ingress. Samples were transferred to the laboratory as soon as possible following the documented rainfall events.

Two stream water samples were collected from Streets Creek on the Macalister Range, approximately 1 km upgradient from the Kuranda Range Road (Figure 2-22). Samples were collected using polyethylene bottles rinsed with dilute HCl.

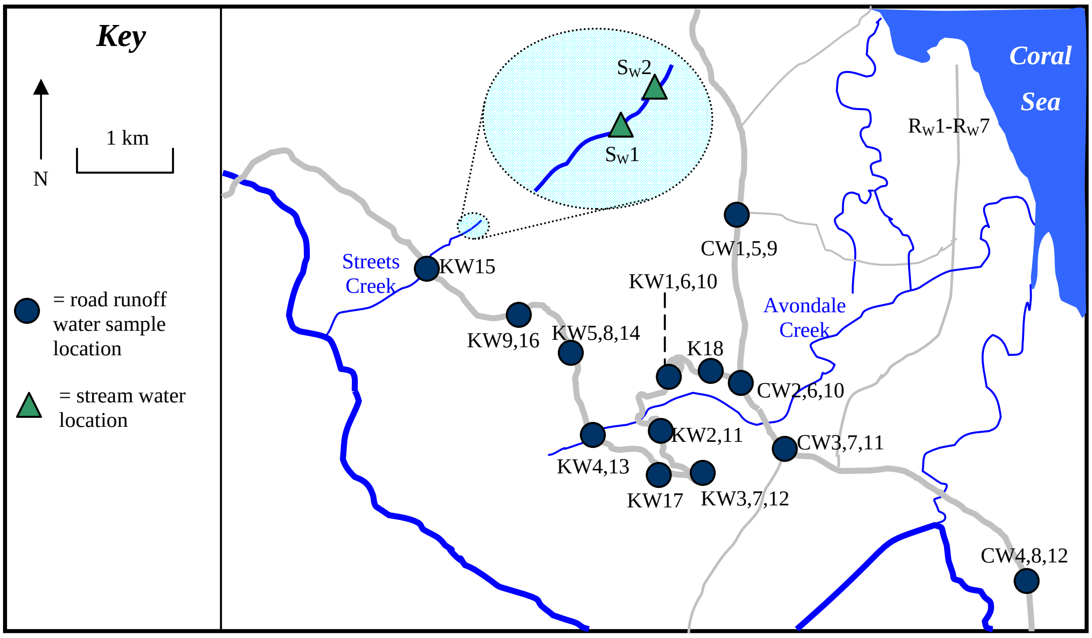


Figure 2-22: Road runoff water and stream water sample locations.

Finally, seven rainwater samples were collected from Yorkeys Knob, north of Cairns (Figure 2-22). The details of these samples, including their AMG coordinates, are given in Appendix A.

2.5.2 Sample processing and chemical analyses

The samples acquired in February 2003 were immediately filtered through 0.45 µm Millipore filter paper (rinsed with dilute MHCl) into a 10 mL screw-cap plastic test tube. The samples collected in January and November 2004 were subjected to more detailed analyses. Each of the road runoff water samples from these months was split into three equal volumes; one volume was poured directly into a 10 mL screw-cap plastic test tube while another was filtered through 0.45 µm Millipore filter paper into a 10 mL screw-cap plastic test tube. The pH and EC was measured in the remaining volume of each sample. These parameters were recorded using Radiometer Analytical pH/Eh210 and EC210 instruments. The background stream water samples, S_W1 and S_W2, were split into filtered (<0.45 µm Millipore filter paper) and unfiltered portions and the resulting samples were retained in 10 mL screw-cap plastic test tubes.

Filtered and unfiltered water samples were acidified with two drops of 70 % HNO_3 to pH <2 and refrigerated until analysis. All water samples were analysed for Cd, Cu, Pb, Ni and Zn concentrations using ICP-MS at the AAC, Townsville and complete analytical data for individual samples are given in Appendix B.

2.6 Tyre rubber ponding experiment

Two tyres, one car tyre (Goodyear make) and one truck tyre (Goodyear make), were obtained from K-Mart Auto Services and Truck North in Cairns, respectively. The tyres were shredded with a cleaned, stainless steel grater and 1.0 g of grated rubber was obtained from both tyres. Grated rubber from each tyre (0.2 g) was added to five separate test tubes. Ten millilitres of distilled water was poured into the test tubes. In total, there were ten test tubes; each containing 0.2 g of grated tyre rubber and 10 mL of distilled water.

The tubes were capped and shaken end-over-end for 5 minutes. They were then uncapped and left to sit in test tube holders. After 5 minutes, water from one of the test tubes containing car tyre rubber shreds, and from one of the test tubes containing truck tyre shreds, was decanted and filtered through 0.45 µm Millipore filter paper (supplied by Selby Biolab). These decanted water samples were then acidified to a pH <2 with two drops of 70 % HNO_3. The pH, Eh and EC of the solution in each tube were recorded prior to acidification. The same procedure was completed for the liquid in the remaining test tubes following 1 hour, 24 hours, 1 week and 1 month. The decanted water samples were analysed for Cd, Cu, Pb, Ni and Zn concentrations using ICP-MS at the AAC, Townsville. Appendix B lists concentration data for the individual samples.

2.7 Roadside grasses and soils

2.7.1 Collection of grass samples for formal identification

Two samples of the grass species *Melinis repens* (*M. repens*) were collected from adjacent to the Kuranda Range Road and from the Davies Creek area west of Cairns, respectively. The flower and stem tissue of a specimen of *M. repens* is shown in Figure 2-24. Sampled specimens were pressed dry in newspaper. These samples were then sent to the Queensland Herbarium in Brisbane for formal identification. Records of identification of the samples are included in Appendix E.

2.7.2 Sampling

Samples of *M. repens* were collected along the Kuranda Range Road. As this species requires direct sunlight, its presence was restricted to the lower section of the Kuranda Range Road. Along this part of the road, the surrounding vegetation is more woodland-dominated than the upper section of the road, which traverses dense rainforest. Samples were collected from seven locations immediately adjacent to the road edge (Figure 2-23). Where possible, grass samples were also taken at a distance of greater than 5 metres from the road edge, although specimens were only observed at distances of 5 metres from the road edge at four locations (Figure 2-23).

Background samples of *M. repens* were acquired from an open grass field near the Davies Creek Access Road (Figure 2-23). This field is an abandoned paddock, located more than 5 km away from the nearest bitumen road and more than 20 km away from any industrial or mine site. Soil samples were collected from each grass sample location. Soils were obtained by shaking the roots of the grass samples. The AMG coordinates for all grass and soil sample locations are given in Appendix A.

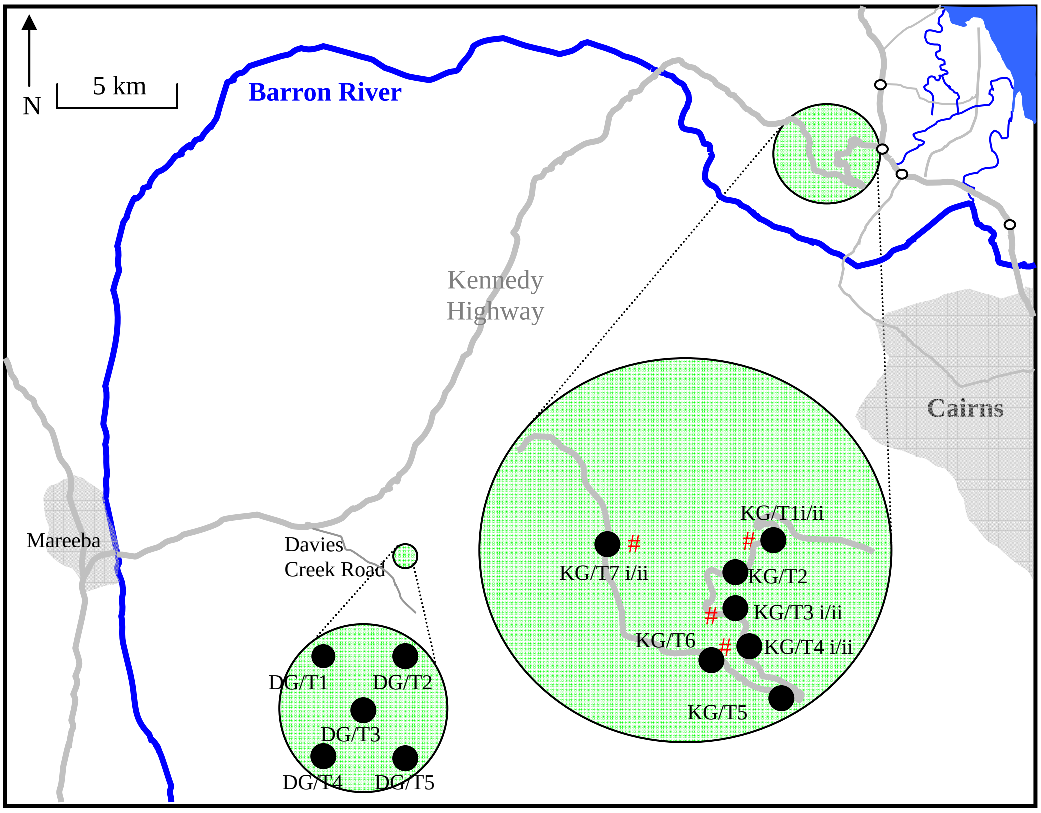


Figure 2-23: Locations of grass and soil samples (*# indicates location (ii) where sample was collected more than 5 m from the road edge as well as immediately adjacent to road edge).*

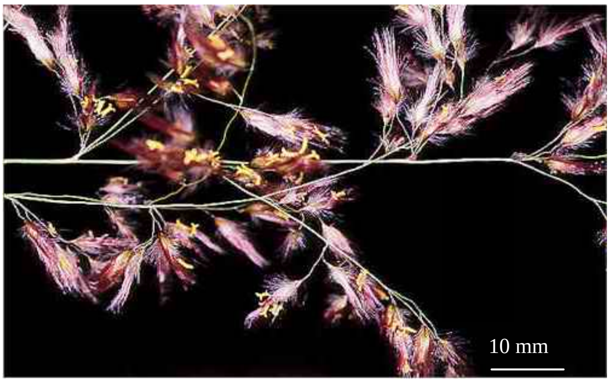


Figure 2-24: Photograph of the stem portion of a *M. repens* specimen, indicating distinctive red/pink colour of flowers (Carr 2005).

2.7.3 Sample processing

Stem and flower tissue from each grass sample were separated from the roots. The samples were thoroughly washed with distilled water following the ICARDA plant analysis manual (2001). Stem and flower and root samples were then weighed out into 10 mL borosilicate glass test tubes. The glass tubes were placed into a borosilicate glass beaker which was transferred into an ashing oven. The grass samples were ashed at 550^0C for 48 hours (ICARDA 2001).

Following cooling, 2 mL of 32 % HCl were poured into each tube; the tubes were left in a fumehood for 24 hours (ICARDA 2001). Two millilitres of 30 % H_2O_2 were subsequently added to each tube and the tubes were left uncapped in a fumehood for 4 hours in order to oxidise the remaining organic-bound heavy metals. The solutions were then poured into 12 mL polyethylene screw-cap test tubes. The solution in each tube was made up to 10 mL with distilled water. Test tubes were centrifuged at 4000 rpm for 20 minutes and the clear extract from each tube was retained. Extracts were submitted for chemical analyses at the AAC, Townsville. Details of the analyses are presented in Section 2.7.6.

Soil samples were oven-dried at 40^oC. These samples were then sieved to <2 mm to remove coarse debris (Sutherland et al. 2000). A portion of each sample was crushed to powder in a chrome steel ring mill and these powdered samples were sent to ALS, Brisbane for chemical analyses. Section 2.7.6 outlines the analytical procedures.

2.7.4 DTPA extractions of soils

Heavy metals were extracted from all soil samples using the DTPA extraction procedure described by Rayment and Higginson (1992). The method of Rayment and Higginson (1992) was strictly adhered to. The extraction procedure is detailed in Appendix C. DTPA extracts were submitted to the AAC, Townsville for chemical analyses and the details of the analyses are described in Section 2.7.6.

2.7.5 Greenhouse trial

Nine hundred grams the composite road sediment sample, KRC_M3 (Appendix A) were placed into a clean Terracotta pot. Seeds of *M. repens,* collected from a herbarium-identified specimen, were planted to a depth of 0.5 cm in the pot in three rows. Approximately five seeds were planted in each row. The above procedure was also carried out for the bulk sample, CRC_M3, from the Captain Cook Highway roundabouts (Appendix A).

The pots were placed outdoors under an awning so that they received direct sunlight for a few hours per day. The sediment in both pots was watered daily with distilled water. After a period of 15 weeks, when the grasses had grown approximately 0.5 m above the sediment surface level, two individual grass specimens were extracted (with roots) from the pot containing sediment of KRC_M3. Only one specimen successfully grew in the CRC_M3 sediment sample and this grass was extricated from the pot. In total, three specimens were obtained; two from the pot containing Kuranda Range Road sediments (L72 and L73, Appendix A) and one from the pot containing Captain Cook Highway roundabout sediments (L74, Appendix A). Stem tissue from each grass sample was separated from the roots. The same procedure for digestion and analysis of these specimens was carried out as specified in Section 2.7.3.

2.7.6 Chemical analyses

All digested plant samples were analysed for Cd, Cu, Pb, Ni and Zn using ICP-MS at the AAC in Townsville. The soils were analysed for Cd, Cu, Pb and Ni by ICP-MS and for Zn by ICP-AES following digestion in $HF\text{-}HNO_3\text{-}HClO_4$, as well as for Pd and Pt by ICP-MS following fire assay (ALS, Brisbane). Concentration data for individual soil and grass samples are shown in Appendix B.

2.8 Remediation laboratory experiments

2.8.1 Experiment design and procedure

The remediation experiments were conducted in two stages. Firstly, a leachate was produced by pouring distilled water through a batch of road sediments. Secondly, proportions of this leachate were added to the various adsorptive materials examined in this research (zeolite, mushroom compost and bentonite). The details of the experiments are discussed forthwith.

Three hundred grams of the composite road sediment sample KRC_M2 were placed into a plastic column. Six hundred millilitres of distilled water were then poured through the column containing the road sediment. The resulting leachate was filtered using Whatman Number 1 filter paper. This leachate was used in three remediation experiments involving zeolite, mushroom compost and bentonite, respectively. The zeolite used in the experiment was clinoptilolite (acquired from Supersorb Environmental, Western Australia). The bentonite granules were obtained from Queensland Bentonite at Miles and the mushroom compost was acquired from Buffalo Raw Materials, Cairns.

The zeolite experiment was performed first. Six 500 mL conical beakers were placed onto a work bench. Fifty grams of zeolite crystals were placed into three of these beakers. The road sediment leachate was split into six equal proportions (approximately 85 mL, noting that some of the distilled water was adsorbed by the sediment) and these volumes were poured into the six conical beakers. One beaker containing only road sediment leachate and no zeolite (i.e. the control experiment) and one beaker containing road sediment leachate and zeolite were sampled immediately after 5 minutes of settling. The two samples were filtered through 0.45 µm Millipore filter, then poured into a plastic 12 mL polyethylene screw-cap test tube and acidified to pH <2 with two drops of 70 % HNO_3. The procedure was repeated for the remaining test and control beakers after 1 hour and 24 hours of settling, respectively (Table 2-4). The same experiment was repeated twice; using bentonite granules and mushroom compost in place of zeolite.

Table 2-4: Design of the remediation experiments.

Solution	*Remediation material*	*Setup*	*Sampling intervals*	*Number of supernatants analysed*
Distilled water with road sediments	*Zeolite*	6 beakers - 3 with zeolite - 3 x control	• 5 minutes • 1 hour • 24 hours	6
	Mushroom compost	6 beakers - 3 with compost - 3 x control	• 5 minutes • 1 hour • 24 hours	6
	Bentonite	6 beakers - 3 with bentonite - 3 x control	• 5 minutes • 1 hour • 24 hours	6

2.8.2 Permeability experiments

Fifty grams of each of the studied materials (zeolite, compost and bentonite) were placed into column tubings underlain by nylon gauze. Two hundred millilitres of distilled water were poured through each column and the time taken for the liquid to pass through the respective materials was measured.

2.8.3 Chemical analyses

All samples from the remediation experiments were analysed for pH prior to acidification. Samples were then analysed for Cd, Cu, Pb, Ni and Zn concentrations through ICP-MS at the AAC, Townsville. Appendix B presents concentration data for all samples obtained from the remediation experiments.

2.9 Quality assurance

2.9.1 Analysis of blanks

A total of 55 blank liquid and solid samples were analysed over the course of the project. These samples included: a) Cape Flattery silica sand samples that had been sieved, crushed in the chrome steel ring mill and oven dried (n = 8); b) distilled water blanks collected in the laboratory experiments (n = 29); c) a distilled water blank analysed with the road runoff water samples (n = 1); d) reagent blanks for the DTPA and EDTA bioavailable solutions (n = 12); and e) reagent blanks for the solutions used in the partial and sequential extractions (n = 4).

The analytical results for the distilled water blanks indicated no significant contamination of the sample media, with the exception of sample QC56 (Appendix D) which was revealed to have become contaminated on arrival to the laboratory. Consequently, results of QC56 were omitted from the data analysis. Average metal values detected in the 29 distilled water samples were: Cd 0.1 µg/L; Cu 1.6 µg/L; Pb 1.2 µg/L; Ni 0.7 µg/L and Zn 11.8 µg/L. Metal values in the 16 reagent blank samples were higher than in the distilled water samples, and this is attributed to the presence of metals in the reagent salts. Despite this, metal values in the reagent blank samples were exceptionally lower (up to10000x) than metal concentrations in the sediment and soil extract samples (Appendix B). The analytical results for all blank samples are given in Appendix D.

2.9.2 Precision

Precision, referring to the repeatability of a measurement, was determined by analyses of replicated samples. “Acceptable” levels for differences in concentrations for compounds between parent and replicate samples are presented in Australian Standard Number AS 4482.1 (Australian Standards 2003). The “acceptability” of these levels is determined by calculating relative percent differences (RPDs) between parent and duplicate concentrations, in the following way:

$$RPD = ([M]_p - [M]_d)/ \{([M]_p + [M]_d)/2\} \times 100 \qquad \textbf{(Equation 2-1)}$$

where $[M]_p$ = metal concentration in the parent sample and $[M]_d$ = metal value in the duplicate sample. RPDs of 50 % or less, for a given contaminant, are deemed acceptable (Australian Standards 2003). Results from Table 2-5 indicate that most RPDs between parent and duplicate samples were in the "acceptable" range for solid and liquid samples, thus indicating strong precision within the laboratory results. A complete summary of results for all parent and duplicate samples is given in Appendix D.

Table 2-5: Percentage of RPDs in the "acceptable" range for solid and liquid samples.

	Percentage of analytes in the "acceptable" range (<50 % RPD)
Solid (n = 41)	90 %
Liquid (n = 64)	96 %

2.9.3 Accuracy

Accuracy of the laboratory's results was determined by analysis of a reference material. A portion of reference material GXR-3 was submitted on seven occasions to ALS (Brisbane) for total metal analysis (Cd, Cu, Pb, Ni and Zn) by ICP-MS following digestion in $HF\text{-}HNO_3\text{-}HClO_4$. The compilation values in Table 2-6 represent the average concentrations for the heavy metals in this sample.

Heavy metal values for only six of the seven analyses of this reference sample, given by ALS, are presented in Table 2-6. This is because on one occasion, in August 2004, the laboratory reported values for the sample were well outside the expected range, with such large variation attributed to contamination of the sample rather than to laboratory error. This was confirmed by re-analysis of the sample by ALS. Consequently, results of the analysis of this sample were not included in the quality control dataset.

Overall, the laboratory reported values for the reference sample showed minimal variance over the various rounds of analysis, as indicated by the consistently low standard deviation values for each metal (Table 2-6). Accuracy of the laboratory’s analysis was deemed to be strong with the mean value for each metal very similar or equal to the compilation values recorded for the corresponding heavy metals (Table 2-6). Only Ni and, to a lesser extent Pb, concentrations were consistently below the compilation values (Table 2-6). A complete summary of results for the standard reference sample GXR-3 as reported by ALS is given in Appendix D.

Table 2-6: Laboratory reported heavy metal concentrations for standard reference sample GXR-3 compared with compilation values.

	Compilation values (mg/kg)	**Values (mg/kg) determined by laboratory results reported in this project (n = 6)**			
		Mean	*Standard deviation*	*Maximum*	*Minimum*
Cd	0.3	0.3	0.02	0.32	0.28
Cu	15	12.08	2.37	16.8	10.6
Pb	15	13.4	1.11	14.7	12
Ni	60	45.43	3.44	49.8	40.4
Zn	207	189.33	25.35	232	154

2.9.4 Detection limits

The lower detection limits for ICP-MS allowed resolute analysis of trace metal concentrations in the solid and liquid samples analysed in this study. Only Cd in the liquid samples was regularly below the lower detection limit associated with ICP-MS (Table 2-7, 2-8). ICP-AES was required for analysis of Zn in solid samples because its concentrations were commonly above the upper detection limit associated with ICP-MS (Table 2-7).

Table 2-7: Detection limits for solid samples. Wt % = 10g/kg.

	Instrument type					
	ICP-MS (given by ALS)		***ICP-AES (given by ALS)***		***XRF (given by the AAC)***	
	Lower	*Upper*	*Lower*	*Upper*	*Lower*	*Upper*
Cd (mg/kg)	0.01	500	1	1000	-	-
Cu (mg/kg)	0.2	10000	2	50000	3	2360
Pb (mg/kg)	0.2	10000	2	50000	10	133
Ni (mg/kg)	0.2	10000	2	50000	3	2360
Zn (mg/kg)	0.2	500	2	10000	3	260
Al (wt %)	-	-	-	-	0.01	15
Ca (wt %)	-	-	-	-	0.01	15
Fe (wt %)	-	-	-	-	0.01	50
Mn (wt %)	-	-	-	-	0.005	50
S (wt %)	-	-	0.1	500	-	-
C (wt %)	-	-	0.1	500	-	-
Pd (µg/kg)	0.001	1	1	1000	-	-
Pt (µg/kg)	0.0005	1	1	1000	-	-

Table 2-8: Detection limits for liquid samples.

	Instrument			
	ICP-MS (given by the AAC)		***ICP-AES (given by the AAC)***	
	Lower	*Upper*	*Lower*	*Upper*
Cd (μg/L)	0.05	50	0.5	1000
Cu (μg/L)	0.10	10000	1	50000
Pb (μg/L)	0.05	10000	0.5	50000
Ni (μg/L)	0.10	10000	1	50000
Zn (μg/L)	0.10	500	5	10000
Al (mg/L)	-	-	0.5	10000
Ca (mg/L)	-	-	5	50000
Fe (mg/L)	-	-	100	50000

2.10 Statistical methods

Statistical analyses were performed using the SPSS 11.5 software package. Correlation analyses were performed using Pearson's Correlation test. Values were log-normalised prior to the calculation of any correlation coefficients. Additionally, the samples-paired T test was used to determine significant differences in means between groups of data. p values <0.05 were considered statistically significant.

Chapter 3 Traffic-derived metals within road sediments

3.1 Introduction

Road sediments are loose solids that settle and accumulate on road edges. These solids commonly comprise: a) air blown dust particles; b) dust and soil mobilised by vehicular traffic; c) eroded rock and soil material transported by gravity and/or road runoff waters; d) particles from road-surface wear; e) organic debris; and f) abraded vehicle parts (Sansalone and Buchberger 1997; Turner et al. 2001; Varrica et al. 2003). Road sediments are important sinks for heavy metals and PGEs which are generated from a variety of sources within the road environment (Chapter 1). These sediments that settle on road surfaces constitute the most immediate environmental sink for traffic-derived metals. It is critical to understand the concentrations and distributions of traffic-derived heavy metals and PGEs in road sediments in order to evaluate their environmental fate.

The composition of road sediments can vary markedly between locations due to the variable nature of their sources. However, road sediments from most locations in the world tend to include at least some minerals of the surrounding rocks, soils and sediments (Harrison et al. 1981; Fernandez and Galarraga 2001; Varrica et al. 2003; Sutherland et al. 2004). These primary mineral components may contribute varying trace amounts of heavy metals and PGEs. However, it is really the presence and relative abundances of secondary minerals within these sediments that can control the behaviour and mobility of traffic-derived metals. The relative abundances of carbonates, clays, Al-Fe-Mn oxides/oxyhydroxides and organic matter in road sediments play a crucial role in the solid-phase hosting of heavy metals and PGEs (Harrison et al. 1981; Parker and Rae 1998; Wang et al. 1998).

The accumulation of elevated metal concentrations in road dusts and sediments along busily trafficked roads has been well documented (Fernandez and Galarraga 2001; Sures et al. 2001; Sutherland and Tolosa 2001; Birch and Scollen 2003; Sezgin et al. 2003; Varrica et al. 2003). Yet, investigations into the grain size distribution and the solid-phase speciation of these sediment-hosted metal contaminants have been conducted by few researchers (Harrison et al. 1981; Fergusson and Ryan 1984; Viklander 1998; Wang et al. 1998). These studies have commonly employed sequential extraction procedures to determine the hosting of metal contaminants by road sediments. Anthropogenic metals have been documented to occur in the most readily extractable fraction in these sediments (Sutherland et al. 2004). However, problems associated with extraction procedures, most notably readsorption, often limit conclusions that may be drawn from this technique (Turner et al. 2001). Therefore, studies that incorporate a number of analytical techniques, rather than relying solely on sequential or partial extraction methods, provide the most comprehensive insight into metal contamination of road sediments.

This chapter aims to document the concentrations, distributions and siting of heavy metals (Cd, Cu, Pb, Ni, Zn) and PGEs (Pd, Pt) in road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts. Sequential and partial extractions were performed on the sediments as a preliminary indicator of sediment fraction/metal relationships. Moreover, correlation matrices of the geochemical data were calculated in order to further evaluate the association of heavy metals and PGEs with organic matter as well as Al, Fe and Mn oxides, hydroxides and oxyhydroxides.

3.2 Methods of analysis

Road sediments were collected from the Kuranda Range Road and the Captain Cook Highway roundabouts during several sampling events between October 2002 and August 2004 (refer to Chapter 2 – Section 2.4.1 for sample collection details and Appendix A for sample ID descriptions). The road sediments were dried, sieved to less than 2 mm and analysed for their total Cd, Cu, Pb, Ni, Zn, Pd and Pt contents at ALS, Brisbane (Chapter 2 – Section 2.4.7.1). A number of these samples (indicated in Appendix A) were also analysed for their C_{org} and C_{carb} contents at ALS, Brisbane, as well as their Al, Fe and Mn oxide/oxyhydroxide values at the AAC, Townsville (Chapter 2 – Section 2.4.7.1).

Additionally, composite road sediment samples (described in Chapter 2 – Section 2.4.3) were sieved to 10 different size fractions: >4 mm, 4 mm – 2 mm, 2 mm – 1 mm, 1 mm – 500 µm, 500 µm – 250 µm, 250 µm – 106 µm, 106 µm – 75 µm, 75 µm – 63 µm, 63 µm – 38 µm and <38 µm. Each fraction was analysed for its total metal (Cd, Cu, Pb, Ni, Zn, Pd and Pt) as well as C_{org} content at ALS, Brisbane (Chapter 2 – Section 2.4.7.1).

XRD and SEM-EDS analyses were conducted on composite road sediment samples (Chapter 2 – Section 2.4.4). The analyses were performed at the AAC, Cairns. Further to this, composite road sediment samples taken from the Kuranda Range Road and the Captain Cook Highway roundabouts were subjected to sequential and partial extractions (refer to Chapter 2 – Section 2.4.5). The liquid extracts were submitted to the AAC, Townsville, for determination of their Cd, Cu, Pb, Ni and Zn concentrations (Chapter 2 – Section 2.4.7.2).

Finally, background stream sediments were acquired upgradient of roads in Avondale Creek and Streets Creek on the Macalister Range (refer to Chapter 2 – Section 2.4.1). The sediments were dried, sieved to <2 mm and analysed for their total Cd, Cu, Pb, Ni, Zn, Pd and Pt values at ALS, Brisbane (Chapter 2 – Section 2.4.7.1). Additionally, three of the stream sediment samples (Appendix A) were analysed for their C_{org} levels at ALS (Chapter 2 – Section 2.4.7.1).

3.3 Results

3.3.1 Total heavy metal and PGE concentrations in road sediments

Total metal concentrations in the road sediment samples are presented in Table 3-1. Specific concentration values for the individual road sediment samples are presented in Appendix B.

Of all the metals analysed, Pd, Pt and Cd had the lowest concentrations. The median values for these metals were all below 1 mg/kg (Table 3-1). Copper, Pb and Ni were present in considerably higher levels, exhibiting median values between 30 mg/kg and 120 mg/kg (Table 3-1). Zinc, however, was the most abundant metal detected in the studied road sediments (Table 3-1). Median Zn concentrations in the sediments collected from the Kuranda Range Road and the Captain Cook Highway roundabouts were 852 mg/kg and 619 mg/kg, respectively.

Differences between the minimum and maximum values were extremely variable for the individual metals in the road sediments (Table 3-1). The narrowest concentration range was evident for Ni (24.5 mg/kg - 94 mg/kg, Table 3-1). In contrast, the largest variations between minimum and maximum values were displayed by Pd and Pt (Table 3-1). The road sediments sourced from the Kuranda Range Road exhibited more disparate extremities in metal values than the sediments taken from the Captain Cook Highway roundabouts (Table 3-1).

Temporal trends in metal concentrations in the road sediments were determined and the results are given in Figure 3-1. Due to the fact that no sediments were taken from the Captain Cook Highway roundabouts in August 2003, data acquired from this sampling episode are excluded from Figure 3-1.

The results indicate that Pb and Pd values in road sediments from the Kuranda Range Road decreased slightly over the three years (Figure 3-1). A more pronounced decrease was observed for Pb levels in sediments from the Captain Cook Highway roundabouts (Figure 3-1). Cadmium levels gradually increased in the Captain Cook Highway roundabout sediments over time, while Cd concentrations in the Kuranda Range Road sediments showed no clear trend (Figure 3-1).

Nickel levels in the sediments from the Kuranda Range Road progressively decreased from October 2002 to August 2004, although Ni values in the Captain Cook Highway roundabout sediments displayed no obvious patterns (Figure 3-1). By comparison, Zn levels in the Kuranda Range Road sediments steadily increased over the sampling period (Figure 3-1). However, Zn concentrations in the Captain Cook Highway roundabout sediments displayed negligible fluctuations from October 2002 to August 2004 (Figure 3-1). Platinum levels diminished sharply in the Captain Cook Highway roundabout sediments, yet Pt concentrations showed minor changes over the sampling period (Figure 3-1).

Background stream sediments were also analysed for their metal content (Table 3-1). It is important to note that all of these background stream sediments were acquired upgradient of roads. Review of the concentration data in Table 3-1 clearly indicates that stream sediment metal values in Avondale Creek were higher than those levels exhibited by Streets Creek (<2 mm fraction). It was noted that the sediments from Streets Creek were largely composed of coarse-grained (500 – 2000 µm) rock and mineral fragments. In contrast, stream sediments acquired from Avondale Creek were extremely fine-grained (<75 µm) and coated with films of light brown organic matter.

The geochemistry of the studied road sediments has been compared with the geochemistry of the background stream sediments (Table 3-1). Such a comparison demonstrates the relative enrichment of road sediments with particular metals. Metal enrichment factors in the road sediments relative to background stream sediments were calculated from the data and are presented in Table 3-1. Background values were determined by averaging the median metal values for the sediments taken from the two investigated streams: Avondale Creek and Streets Creek. It should be noted that despite disparate metal values exhibited by the Avondale Creek and Streets Creek sediments, these two streams are the major water courses impacted by the Kuranda Range Road. Hence, the metal values in sediments from these streams were used collectively to define ‘background’ concentrations.

Palladium and Pt exhibited the greatest enrichment in the road sediments compared with the background stream sediments (Table 3-2). In contrast, Ni was enriched in the background sediments relative to the road sediments (Table 3-2).

Table 3-1: Heavy metal and PGE concentrations in road sediments collected from the project area from October 2002 to August 2004; background stream sediment metal concentrations are included (all <2 mm fraction). Kuranda Range Road sediments n = 30*. Captain Cook Highway roundabout sediments n = 11. Avondale Creek stream sediments n = 6*. Streets Creek stream sediments n = 8*. Refer to Chapter 2 – Section 2.4.1 for sediment sample collection details. Sediment sample ID descriptions are presented in Appendix A and the data for individual samples are included in Appendix B.

	Road sediments				***Background stream sediments***			
	Kuranda Range Road		Captain Cook Highway roundabouts		Avondale Creek		Streets Creek	
	Median	*Range*	*Median*	*Range*	*Median*	*Range*	*Median*	*Range*
Cd (mg/kg)	0.19	0.05 – 0.44	0.21	0.1 – 1.22	0.13	0.12 – 0.19	0.03	0.02 – 0.04
Cu (mg/kg)	41.7	19.2 – 179	57.4	32 – 121	56.6	45.6 – 82.1	21.8	13.8 – 30.9
Pb (mg/kg)	53.3	11.8 – 422	115	44.3 – 214	12.1	9 – 13.2	21.9	16 – 25.1
Ni (mg/kg)	38.8	24.5 – 94	34	29.6 – 40.4	93	70.6 – 124	13.1	12.1 – 17.1
Zn (mg/kg)	852	112 – 3320	619	377 – 1000	98.5	84 – 116	28.5	20 – 34
***Pd (μg/kg)**	34.5	1 – 269	99	43 – 923	3	2 – 4	1	<1 – 1
***Pt (μg/kg)**	86.1	2.1 – 438	152	66.4 – 1050	3.1	2.3 – 3.9	<0.5	<0.5 – 0.6

**For Pd and Pt in Kuranda Range Road sediments, n = 24; in Avondale Creek sediments, n = 2; in Streets Creek sediments, n = 4.*

Table 3-2: Enrichment factors for median metal values in road sediments relative to background stream sediments.

	Kuranda Range Road sediments	***Captain Cook Highway roundabout sediments***
Cd	1.6x	1.8x
Cu	1.1x	1.5x
Pb	3.1x	6.8x
Ni	0.7x	0.6x
Zn	13.4x	9.7x
Pd	17.3x	49.5x
Pt	46.5x	82x

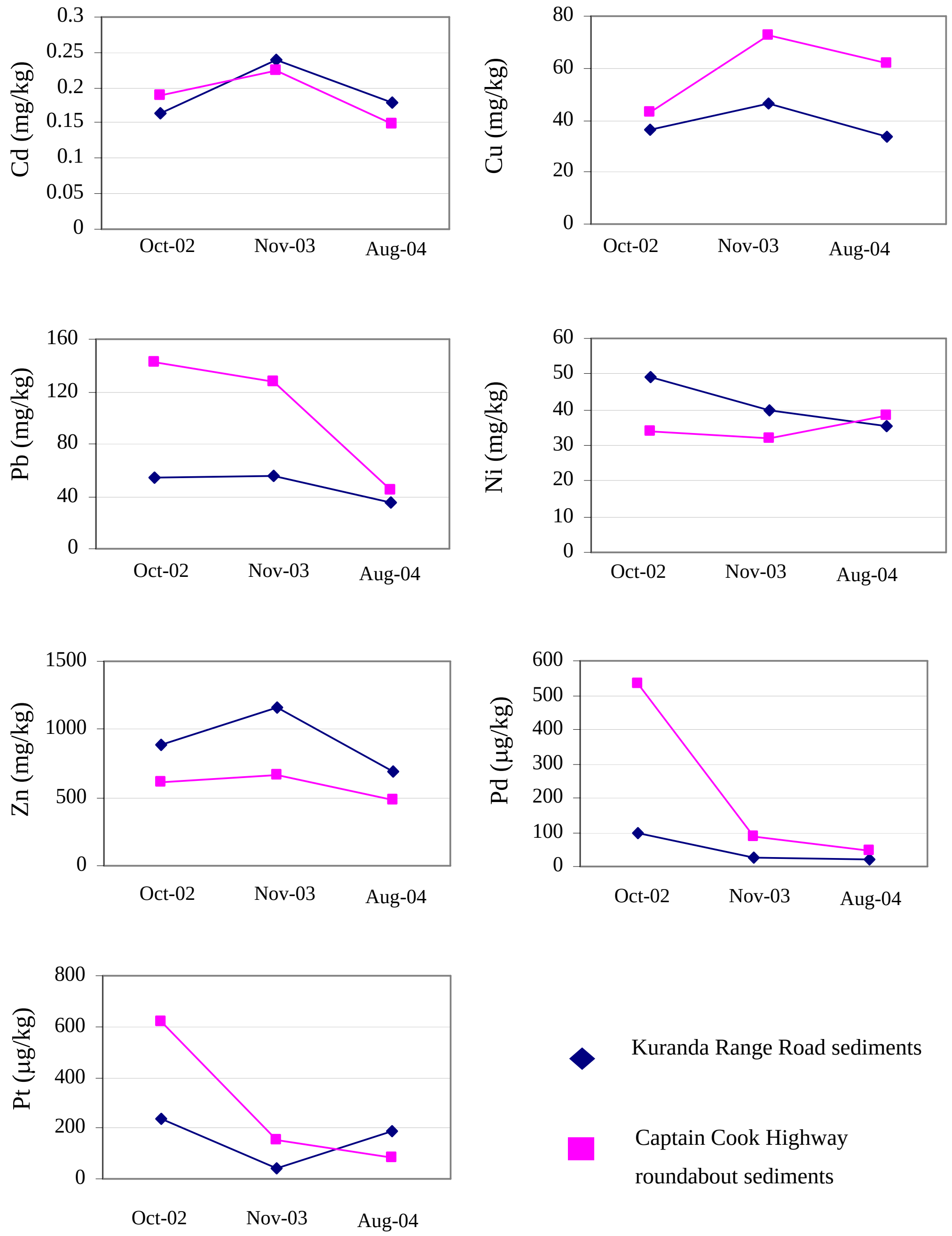


Figure 3-1: Median heavy metal and PGE concentrations in road sediments collected from the project area over three discrete time intervals. For the samples collected from the Kuranda Range Road: n = 6 for Oct 02, n = 9 for Nov 03 and Aug 04*. For the samples collected from the Captain Cook Highway roundabouts: n = 4 for Oct 02 and Nov 03, n = 3 for Aug 04. **For Pd and Pt in Kuranda Range Road sediment samples, n = 3 in Aug 04.*

3.3.2 Distribution of heavy metals in size fractions of road sediments

3.3.2.1 Particle-size distribution of the road sediments

The particle-size distribution of one composite road sediment sample from the Kuranda Range Road (KRC_M1) and one composite sample from the Captain Cook Highway roundabouts (CRC_M1) was determined (sample details are given in Appendix A and concentration data in Appendix B). The resulting particle-size distribution profiles for the representative samples are shown in Figure 3-2.

The fine particles (<106 µm) constituted less than 10 % of the total weight of sediments collected from both the Kuranda Range Road and Captain Cook Highway roundabouts (Figure 3-2). However, major differences in weight distribution for the two profiles were observed in the medium to coarse-grained size fractions. Those particles with diameters 106 µm to 1000 µm (termed medium particles here for convenience) contributed approximately 50 % of the total weight of the Kuranda Range Road sediments. In contrast, the medium size particles constituted approximately 70 % of the total weight of the Captain Cook Highway roundabout sediments (Figure 3-2).

In the case of the Kuranda Range Road sediments, the coarse particle fraction (1000 µm to >4000 µm) supplied about 40 % of the total sediment weight. By comparison, the coarse particle fraction comprised ca. 20 % of the total weight of the Captain Cook Highway roundabout sediments (Figure 3-2).

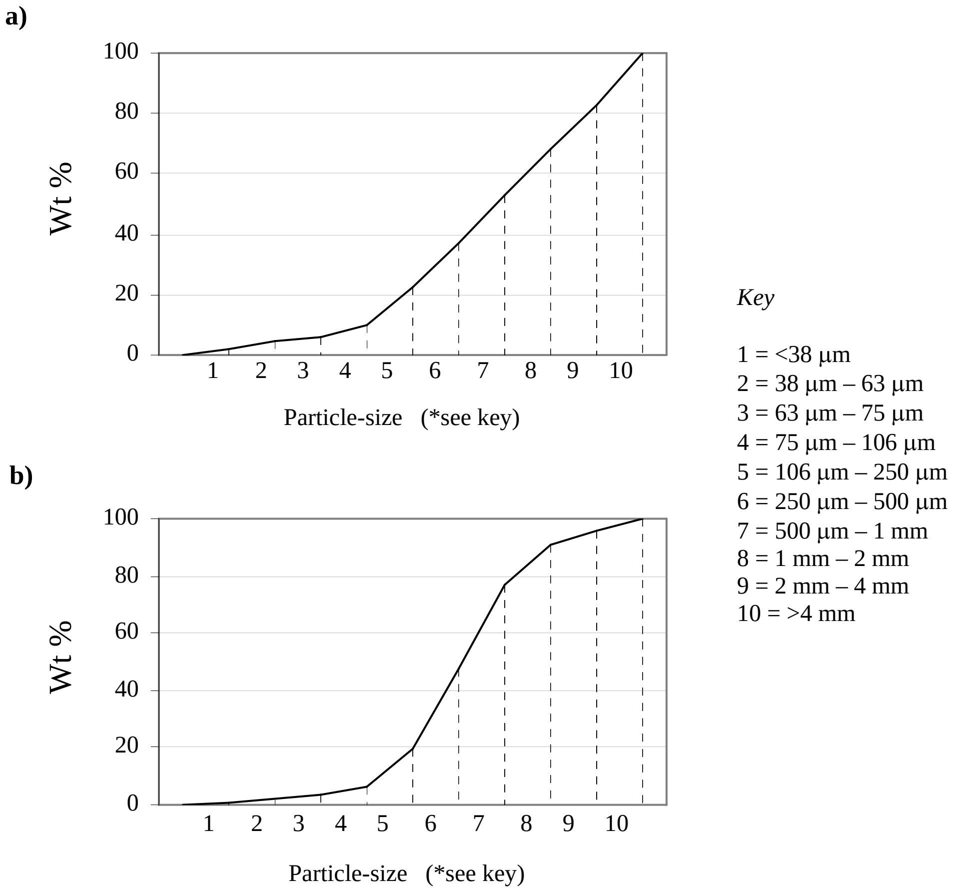


Figure 3-2: Particle-size distribution profiles for two composite road sediment samples from: a) the Kuranda Range Road (KCR_M1) (October 2002); and b) the Captain Cook Highway roundabouts (CRC_M1) (October 2002). Refer to Chapter 2 – Section 2.4.3 for composite sample details. ID for composite samples are given in Appendix A.

3.3.2.2 Particle-size distribution of heavy metals within the road sediments

Heavy metal values were analysed in the individual particle-size fractions of the composite road sediment samples (KRC_M1 and CRC_M1) and the data are presented in Figure 3-3. The results revealed that the metals were commonly most concentrated in the medium to fine-grained particles (<250 µm) within the road sediments. Specifically, it was observed that: a) Cd and Zn were concentrated in the medium-sized particles (250 µm to 106 µm) within the Kuranda Range Road sediments; b) Cd and Zn were most abundant in the fine-grained fraction (<106 µm) of the Captain Cook Highway roundabout sediments; c) Cu and Pb concentrations increased regularly with decreasing particle size in the Kuranda Range Road sediments; d) Cu and Pb were concentrated in the medium to fine particles (<250 μm) in the Captain Cook Highway roundabout sediments; and e) Ni was most concentrated in the coarse particles as well as the fine particles in the Kuranda Range Road and Captain Cook Highway roundabout sediments (Figure 3-3).

Grain-size analyses were also performed on bulk road sediment samples collected in November 2003 (KRC_M2 and CRC_M2). The samples displayed element concentrations and distributions similar to those of samples taken in October 2002 (Figure 3-4).

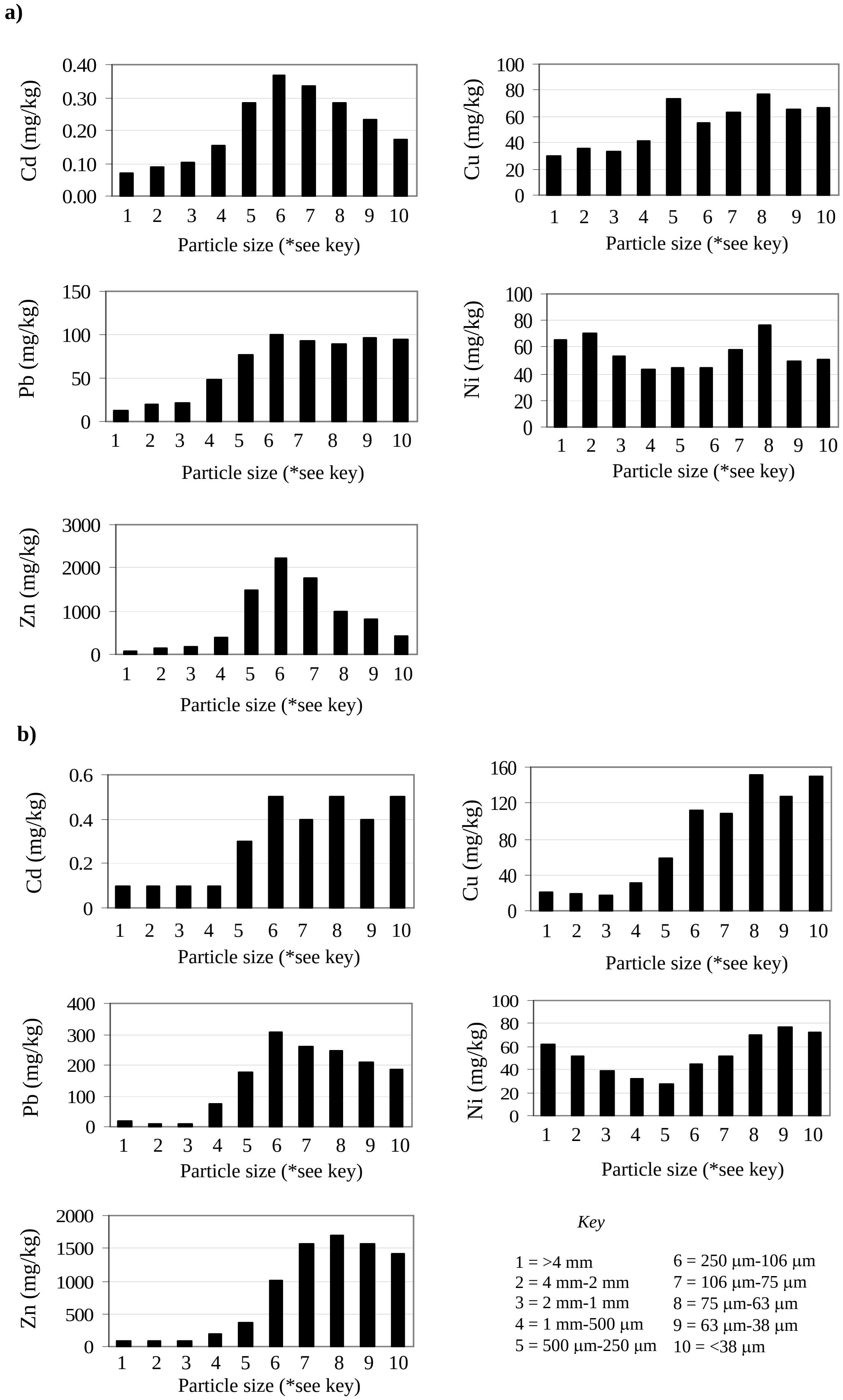


Figure 3-3: Heavy metal concentrations in various particle-size fractions of road sediments from: a) the Kuranda Range Road (KRC$_M$1); and b) the Captain Cook Highway roundabouts (CRC$_M$1) (October 2002). Refer to Chapter 2 – Section 2.4.3 for sieve fraction sample details. ID for sieved road sediment samples are given in Appendix A and the data are presented in Appendix B.

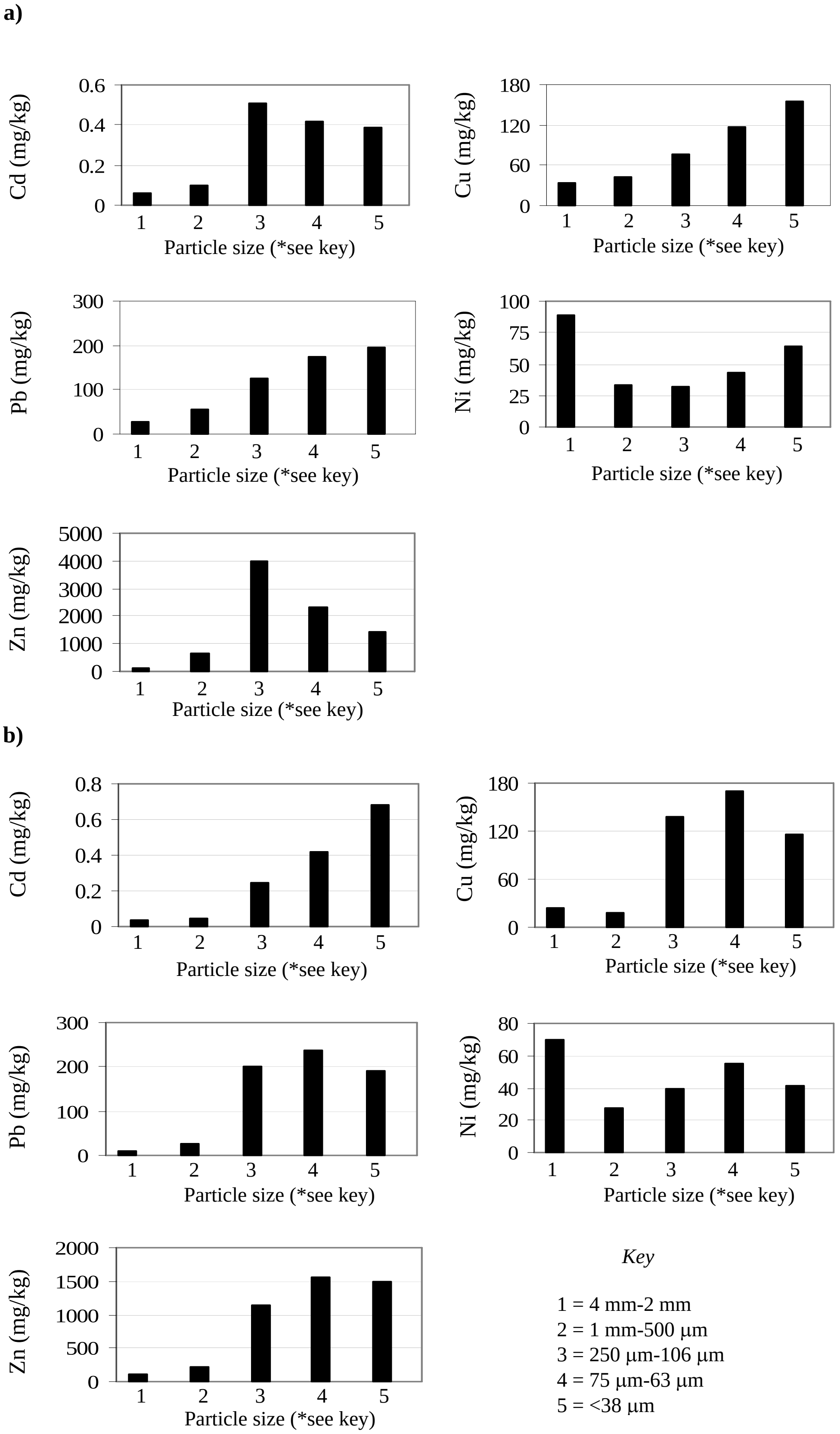


Figure 3-4: Heavy metal concentrations in various particle-size fractions of road sediments from: a) the Kuranda Range Road (KCR$_M$2); and b) the Captain Cook Highway roundabouts (KCR$_M$2) (November 2003). Refer to Chapter 2 – Section 2.4.3 for sieve fraction sample details. ID for sieved road sediment samples are given in Appendix A and the data are presented in Appendix B.

3.3.2.3 Relative masses of heavy metals in various particle-size fractions

The relative masses of heavy metals were determined in each of the various particle-size fractions of bulk road sediment samples KRC_M1 and CRC_M1 by taking into account: a) the concentration of each of the metals in each particle-size fraction; and b) the individual mass of each particle-size fraction. For example, if a Cu concentration of 100 mg/kg was recorded in the 1000 µm to 500 µm fraction of a sediment sample and this fraction weighed 10 g, then the relative mass (Rm) of Cu in this fraction could be calculated as:

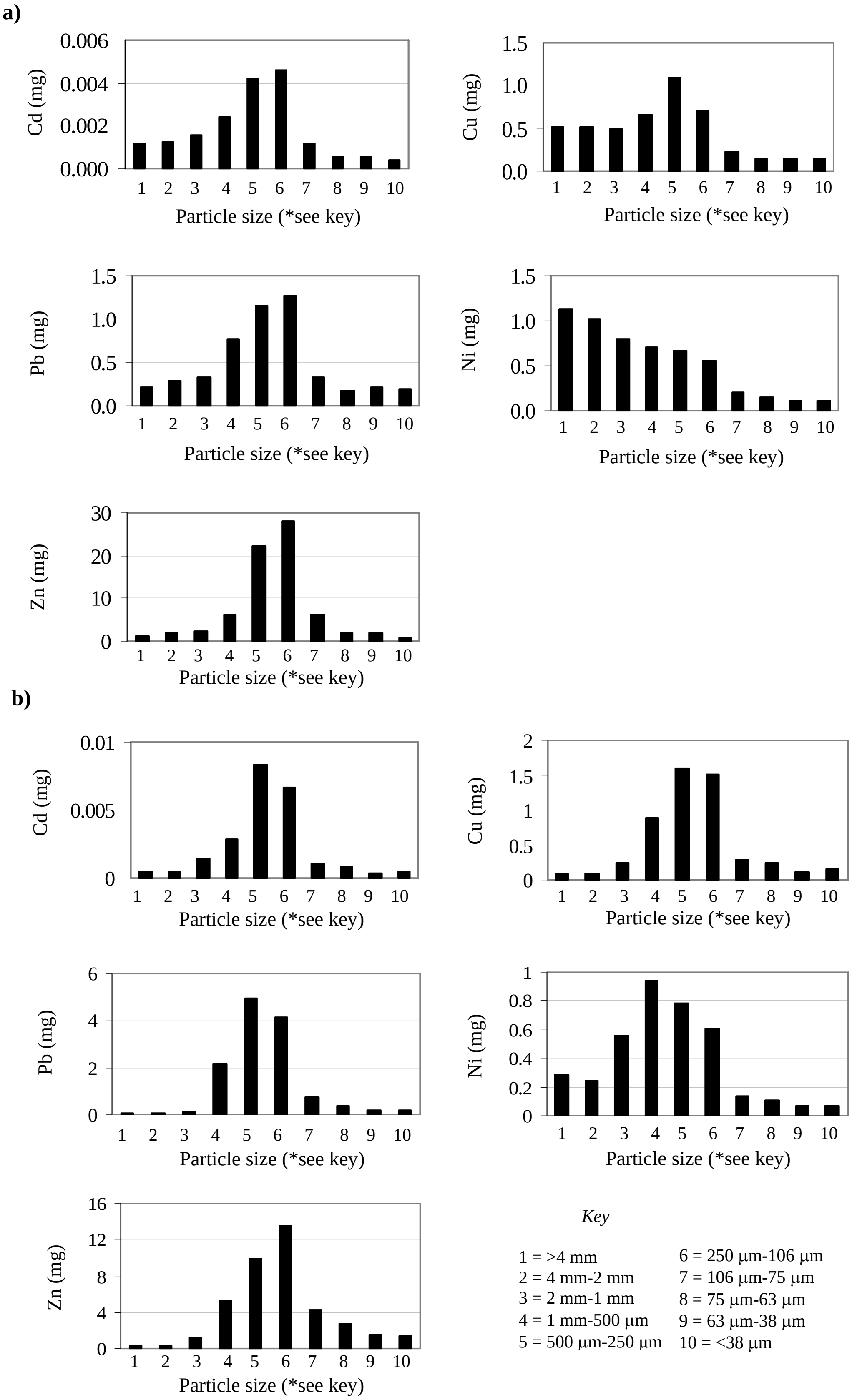
$$Rm\ (g) = [M]_f \times f_m/1000g \qquad \textbf{(Equation 3-1)}$$

where Rm is the relative mass of a metal in the particle fraction, $[M]_f$ is the concentration of the metal in the size fraction (mg/kg) and f_m is the mass of the size fraction (g). For the given example, the relative mass of Cu in the 1000 µm to 500 µm particle fraction can be calculated as:

$$Rm(Cu) = 100mg/kg \times 10g/1000g$$
$$Rm(Cu) = 1\ mg.$$

The relative masses of heavy metals in the various particle-size fractions indicate that the medium-grained particles (500 µm to 106 µm) hosted the greatest abundances of Cd, Cu, Pb and Zn in the road sediments from the Kuranda Range Road and the Captain Cook Highway roundabouts (Figure 3-5). The coarser-grained particles (>500 µm) accommodated the greatest abundances of Ni, particularly in the Kuranda Range Road sediments.

Relative metal masses were also calculated for bulk sediment samples KRC_M2 and CRC_M2. Similar trends to those determined for the October 2002 road sediments were noted for these road sediments acquired in November 2003 (Figure 3-6).



Key

1 = >4 mm
2 = 4 mm-2 mm
3 = 2 mm-1 mm
4 = 1 mm-500 µm
5 = 500 µm-250 µm
6 = 250 µm-106 µm
7 = 106 µm-75 µm
8 = 75 µm-63 µm
9 = 63 µm-38 µm
10 = <38 µm

Figure 3-5: Relative masses of heavy metals within various particle-size fractions of sediments from: a) the Kuranda Range Road (KRC$_M$1); and b) Captain Cook Highway roundabouts (CRC$_M$1) (October 2002) * *In 100 g of sediment.*

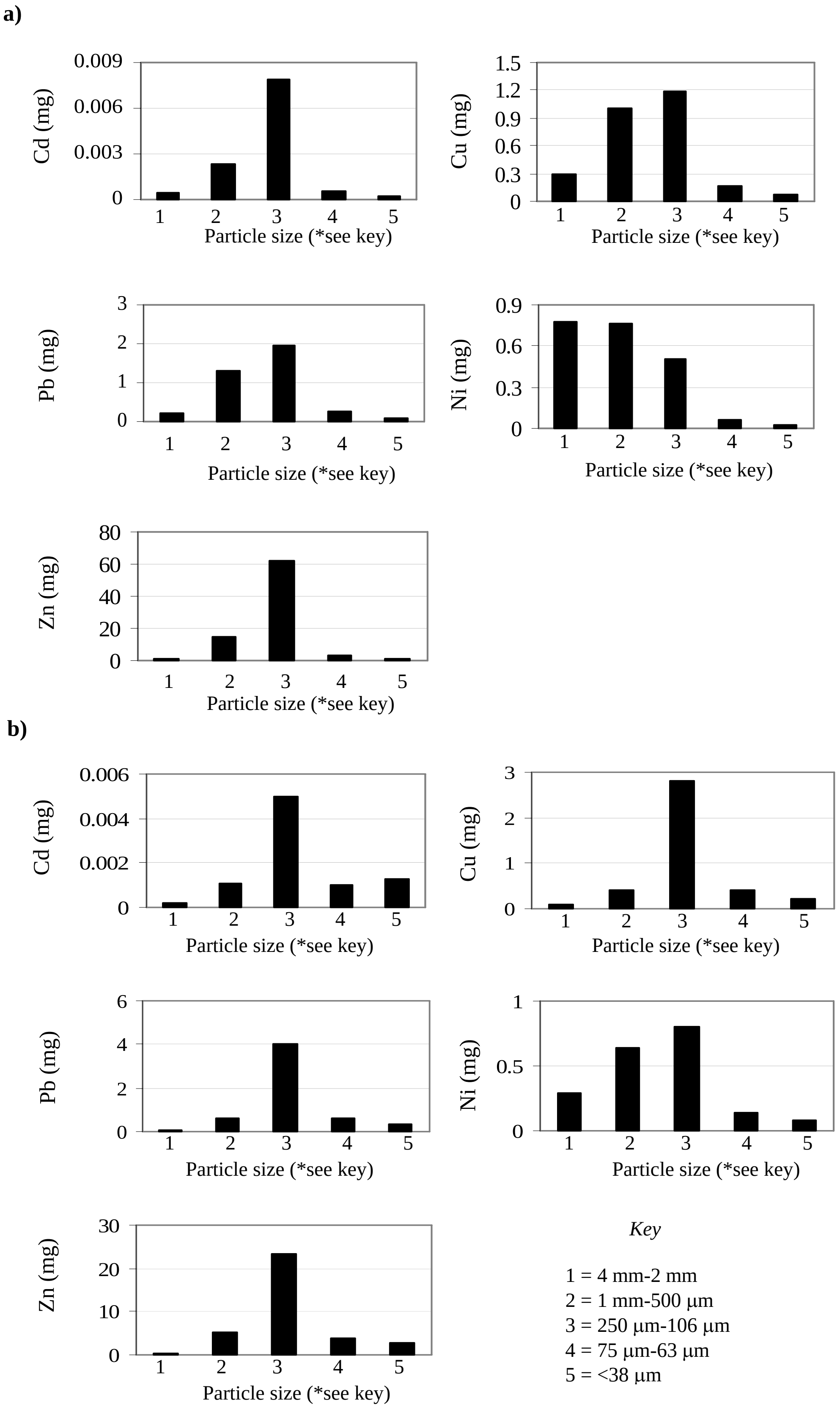


Figure 3-6: Relative masses of heavy metals within various particle-size fractions in road sediments from: a) the Kuranda Range Road (KCR$_M$2); and b) the Captain Cook Highway roundabouts (CRC$_M$2) (November 2003) * *In 100 g of sediment.*

3.3.3 PGE particle-size distribution in road sediments

Composite sediment samples sourced from the Kuranda Range Road and the Captain Cook Highway roundabouts in August 2004 (KRC_M3 and CRC_M3, respectively) were sieved and the distribution profiles are given in Figure 3-7 a and b, respectively. The resulting size fractions were analysed for Pd and Pt concentrations and the concentration profiles are given in Figure 3-8.

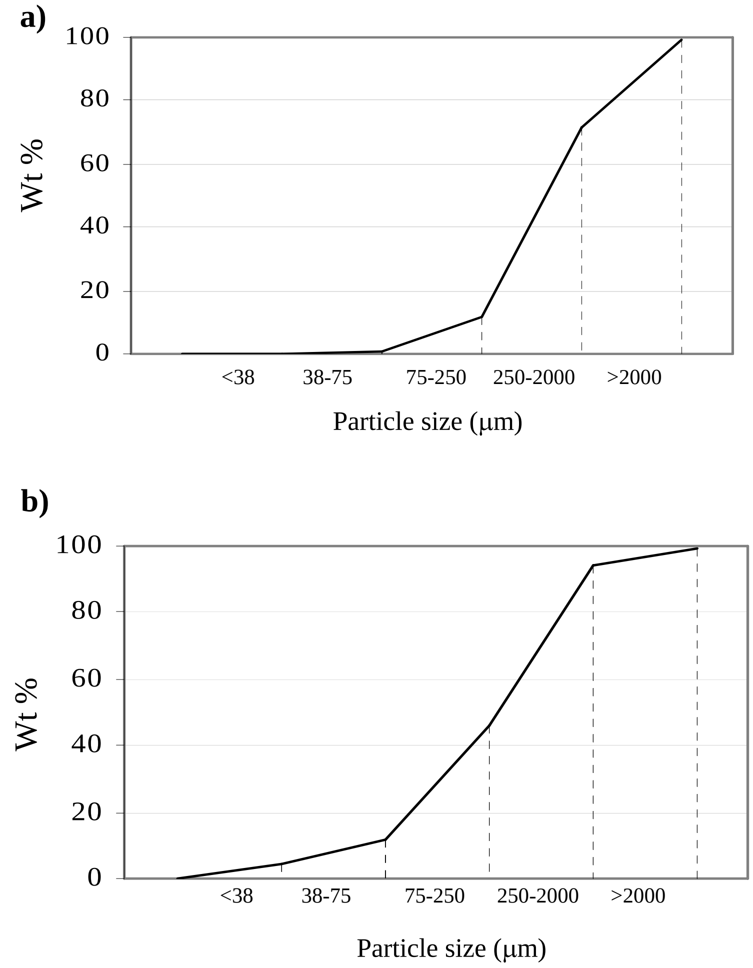


Figure 3-7: Particle-size distribution profiles for road sediments from: a) the Kuranda Range Road (KRC_M3); and b) the Captain Cook Highway roundabouts (CRC_M3) (August 2004). Refer to Chapter 2 – Section 2.4.3 for composite sample details. ID for composite road sediment samples are given in Appendix A.

Palladium and Pt concentrations were lowest in the coarsest fraction (2 mm to 250 μm) of the road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts (Figure 3-8). Furthermore, concentrations of Pd and Pt in the various particle-size fractions of the Kuranda Range Road sediments were generally highest in the finer particle-size intervals (<250 µm) (Figure 3-8). The distribution of Pd and Pt in the Captain Cook Highway roundabout sediments indicates that these PGEs were concentrated in the 250 µm to 75 µm particle-size fraction (Figure 3-8).

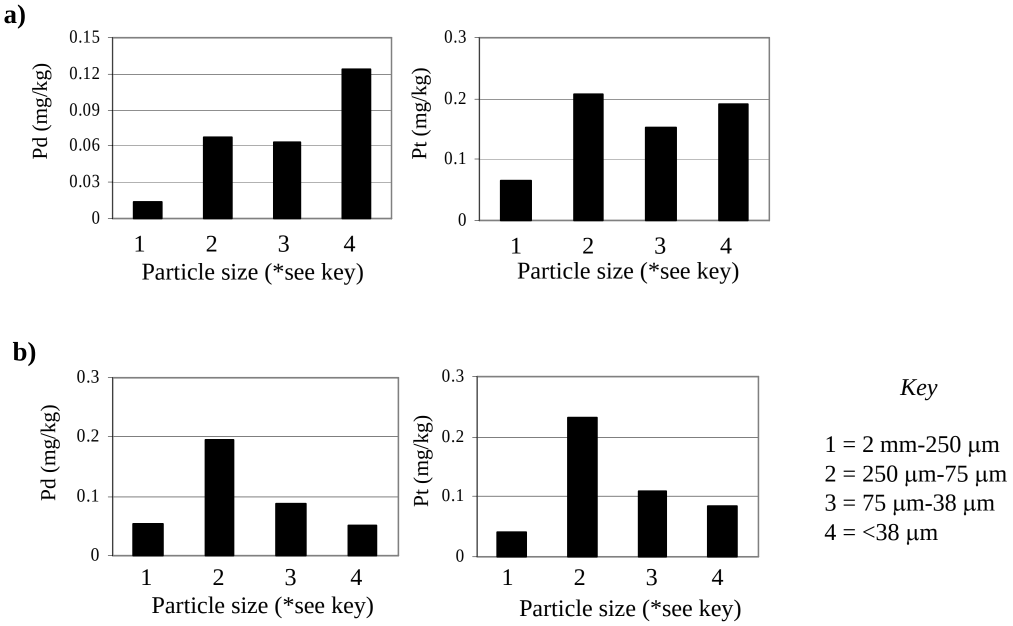


Figure 3-8: PGE concentrations within various particle-size fractions in road sediments from: a) the Kuranda Range Road (KRC_M3); and b) the Captain Cook Highway roundabouts (CRC_M3) (August 2004). Refer to Chapter 2 – Section 2.4.3 for sieve fraction sample details. ID for sieved road sediment samples are given in Appendix A and the data are presented in Appendix B.

3.3.3.1 Relative masses of PGEs in various particle-size fractions

The relative masses of Pd and Pt in each of the size fractions of the road sediments collected in August 2004 were determined using Equation 3-1 (Section 3.3.2.3). Results from Figure 3-9 indicate that, like the heavy metals, Pd and Pt were more abundant in the coarser (2 mm to 250 µm) and medium size (250 µm to 75 µm) fractions than in the very fine material (<38 µm). For the Kuranda Range Road sediments, the relative masses of Pd and Pt were highest in the 2 mm to 250 µm size-fraction. By comparison, the masses of these PGEs reached their maxima in the

250 µm to 75 µm particle-size fraction of the Captain Cook Highway roundabout sediments (Figure 3-9).

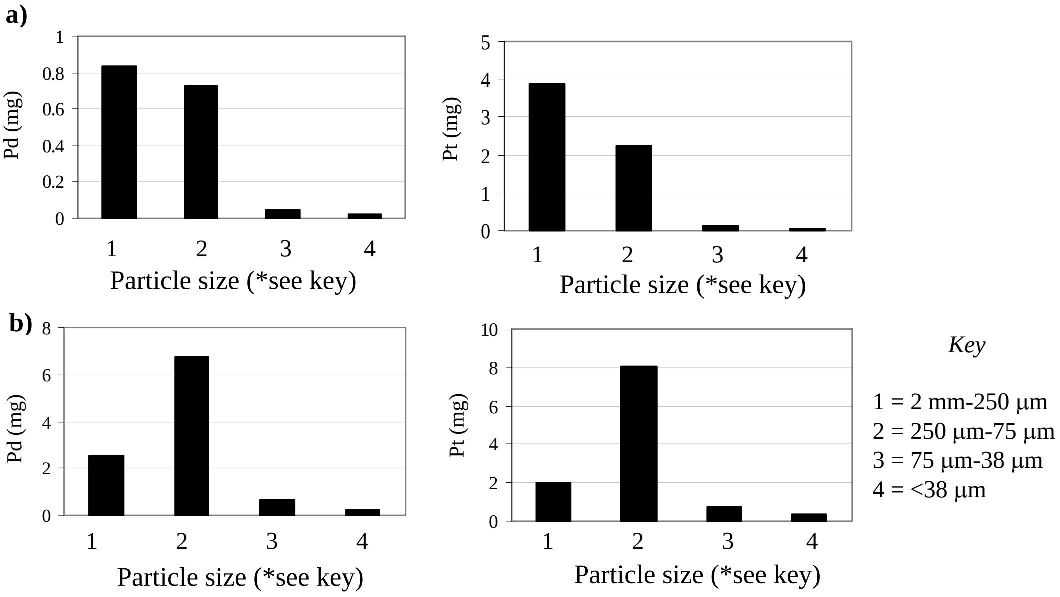


Figure 3-9: Relative masses of Pd and Pt in the various particle-size fractions in road sediments from: a) the Kuranda Range Road (KRC$_M$3); and b) the Captain Cook Highway roundabouts (CRC$_M$3) (August 2004).

3.3.4 Mineralogy and major element geochemistry of road sediments

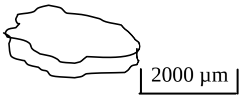
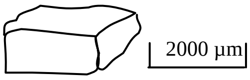
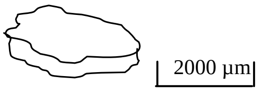
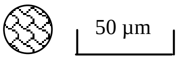
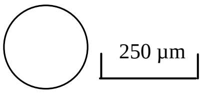
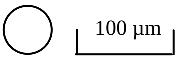
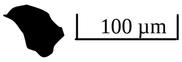
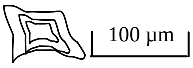
XRD analysis of bulk road sediment samples KRC$_M$1 and CRC$_M$1 revealed major amounts of orthoclase and quartz; and orthoclase, quartz, albite and muscovite, respectively (Appendix G). The presence of aluminosilicates in the road sediments is signified by the high Al_2O_3 concentrations (Table 3-3). While XRD analysis did not reveal any Fe-phases, carbonates or organic matter, their presence is indicated by elevated Fe_2O_3, C_{carb} and C_{org} contents in the sediments (Table 3-3). Comparatively, the MnO values in the analysed sediments are very low; suggestive of traces of secondary Mn phases (Table 3-3). Minor phases may have been overlooked by manual interpretation of the XRD data.

Table 3-3: Major element geochemistry of the road sediments. * = median values. Refer to Chapter 2 – Section 2.4.7.1 for sample analytical details. Appendix A presents sample ID and the data are given in Appendix B.

	C_{org} (wt %)	C_{carb} (wt %)	Al_2O_3 (wt %)	Fe_2O_3 (wt %)	MnO (wt %)
Kuranda Range Road sediments	9.5 (n = 1)	3.0 (n = 1)	7.8* (n = 6)	5.2* (n = 6)	0.08* (n = 6)
Captain Cook Highway roundabout sediments	3.4 (n = 1)	0.9 (n = 1)	5.2* (n = 4)	3.6* (n = 4)	<0.05* (n = 4)

SEM/EDS observations revealed the presence of a variety of particle types and sizes in the studied road sediments (Table 3-4, Figure 3-10). The particles ranged from coarse-grained, primary mineral components (commonly greater than 100 µm in diameter) to very fine, abraded metallic particles (occasionally less than 10 µm in diameter). The matrix of the road sediments was dominated by the presence of tyre rubber shreds, which varied markedly in length but commonly ranged between 250 µm and 100 µm in diameter. The tyre rubber shreds and the fine metallic phases exhibited the most diverse elemental surface chemistry.

Table 3-4: Summary of SEM-EDS observations on road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts. Refer to Chapter 2 – Section 2.4.4 for sample preparation details. SEM-EDS chemistry for various particles is given in Appendix G.

Particle Type	Element peaks (in order of height)	Sketch and size	Description
Primary minerals			
K-feldspar	Si, Al, K, Fe, Ca-Na		Stacked platelet or distorted appearance
Quartz	Si, Ti		Common, varying appearance and size, well-rounded
Plagioclase feldspar	Si, Ca, Na, Al, K, Fe		Similar appearance to K-feldspar
Anthropogenic particles			
Tyre rubber	Si, Al, S, Cl, K, Ca, Fe, P, Mg, Na, Zn		Elongated, strongly textured surface, common distribution
Iron sphere	Fe		Well-rounded, scaly appearance
Reflective glass spheres	Si, Ca, Na		Common distribution
Silica-aluminium sphere	Si, Al		Rare distribution
Titanium-rich road paint flecks	Ti, Fe, Si, Al		Small, dark grains
Metal-rich amorphous phases	Si, Fe, Al, K, Mg, Ti, Zn, Mn, Cl		Plate-like, uncommon

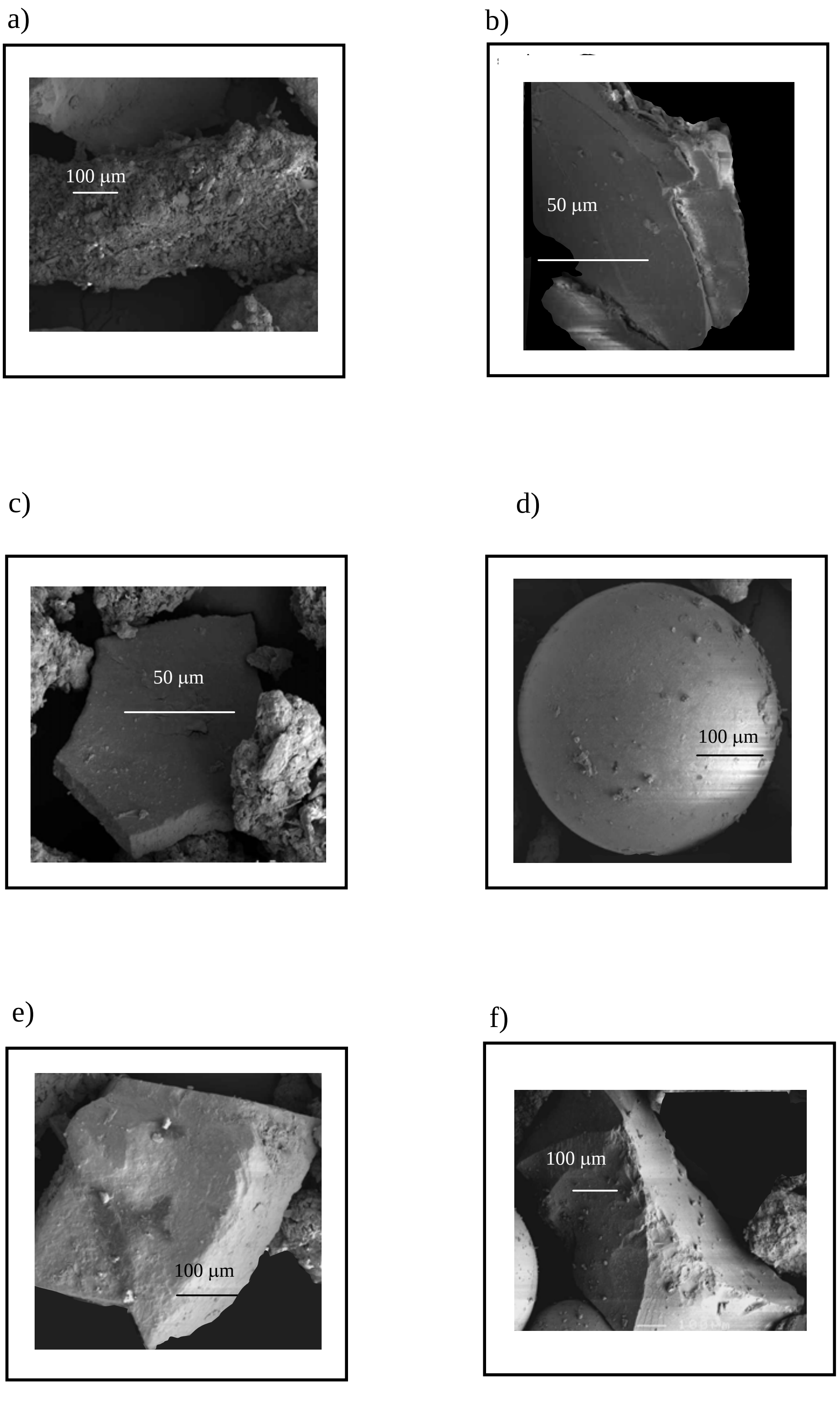


Figure 3-10: Representative SEM photographs of mineral and anthropogenic particles in road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts: a) tyre rubber shred; b) Fe-rich plate; c) Ti-rich paint fleck; d) silica sphere; e) K-feldspar; f) plagioclase feldspar.

3.3.5 Extractions

3.3.5.1 Sequential extraction of metals

The composite road sediment sample collected from the Kuranda Range Road in August 2004 (KRC_M3, Appendix A) underwent sequential extraction following the procedure outlined by Tessier et al. (1979) (Chapter 2 – Section 2.4.5.1). Individual element concentrations detected in the various leachates were recalculated to represent proportional abundances relative to the total metal concentration (formulae given in Appendix C).

Results from the sequential extraction indicate that all analysed metals were primarily associated with residual phases in the road sediments (Figure 3-11). It is also noticeable that Cd, Cu, Pb and Ni were not detected in the oxide/oxyhydroxide fraction in this particular sequential extraction. In contrast, Zn was present in the oxide/oxyhydroxide fraction but was not detected in the organic/sulphide phase. Specific trends for the metals in the various fractions are discussed forthwith.

The residual fraction hosted 35 wt % of Cd, whereas the organic/sulphide fraction accommodated slightly lower Cd concentrations (approximately 33 wt % of total Cd). The carbonate and exchangeable fractions held approximately 20 wt % and 10 wt % of the total Cd content of the road sediments, respectively. Less than 5 wt % of the Cd in these sediments was water-soluble (Figure 3-11).

In comparison, Cu was overwhelmingly present in the residual phase (approximately 82 wt % of total Cu). The organic/sulphide phase was the next most important fraction for Cu, hosting approximately 13 wt % of the total Cu in the road sediments. Much lower amounts of Cu were held by the carbonate phase (Approximately 4 wt % of total Cu). Additionally, exchangeable and water-soluble Cu values were negligible (both less than 1 wt % of total Cu) (Figure 3-11).

Lead was mainly restricted to the residual fraction, with approximately 77 wt % of total Pb detected in this phase. Carbonate minerals accommodated ca. 23 wt % of the total sediment Pb content. Only a very small proportion of Pb (<0.5

wt % of total Pb) was water-soluble. Furthermore, Pb was not present in the exchangeable fraction (Figure 3-11).

An extremely high proportion of the total Ni content of the road sediments was held in the residual fraction (approximately 95 wt % of total Ni). The organic/sulphide, carbonate, exchangeable and water-soluble fractions all hosted less than 2 wt % of Ni in the sediments (Figure 3-11).

The residual fraction yielded the highest Zn concentrations (ca. 58 wt % of total Zn). Lower amounts of Zn were accommodated by carbonate minerals (28 wt % of total Zn), while approximately 10 wt % of Zn was associated with the oxide/oxyhydroxide fraction. Finally, the exchangeable phase hosted less than 5 wt % of total Zn and the water-soluble fraction of Zn amounted to approximately 1 wt % of the total presence of this metal in the studied road sediments (Figure 3-11).

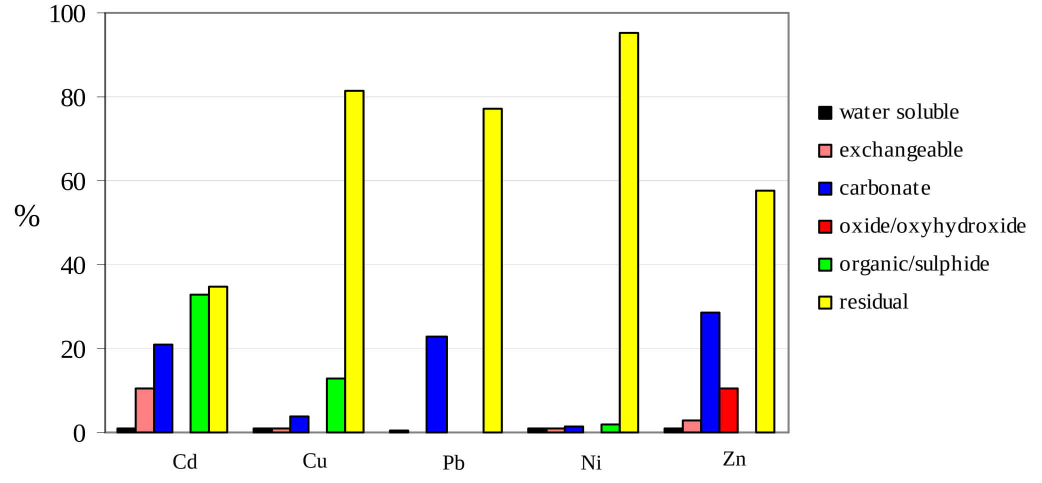


Figure 3-11: Calculated proportions of Cd, Cu, Pb, Ni and Zn in a road sediment sample (KRC$_M$3) from the Kuranda Range Road (sampled August 2004). The individual metal concentrations in the six fractions have been calculated as a percentage of their respective total concentrations in the road sediment. Refer to Appendix A for sample ID for extracts and Appendix B for concentration data.

3.3.5.2 Partial extraction of oxide/oxyhydroxide hosted metals

The citrate-dithionite solution has been designed to target the oxide/oxyhydroxide fraction in soils and sediments (Rayment and Higginson 1992). This extraction was performed to complement the results obtained by the oxide/oxyhydroxide removal step in Tessier et al.'s (1979) sequence.

Results from the citrate-dithionite partial extractions performed on the road sediments confirm that the oxide/oxyhydroxide fraction accommodated only minor amounts of total heavy metals within these sediments (Figure 3-12). Similar trends were observed for the Kuranda Range Road composite sediment sample (KRC_M3) and the Captain Cook Highway roundabout bulk sediment sample (CRC_M3).

Of the heavy metals analysed, Zn was represented in the greatest proportions in the oxide/oxyhydroxide fraction (ca. 4 wt % of total Zn for the Kuranda Range Road sediments and 6 wt % of total Zn for the Captain Cook Highway roundabout sediments) (Figure 3-12). Cadmium was not detected in the extracts (Figure 3-12).

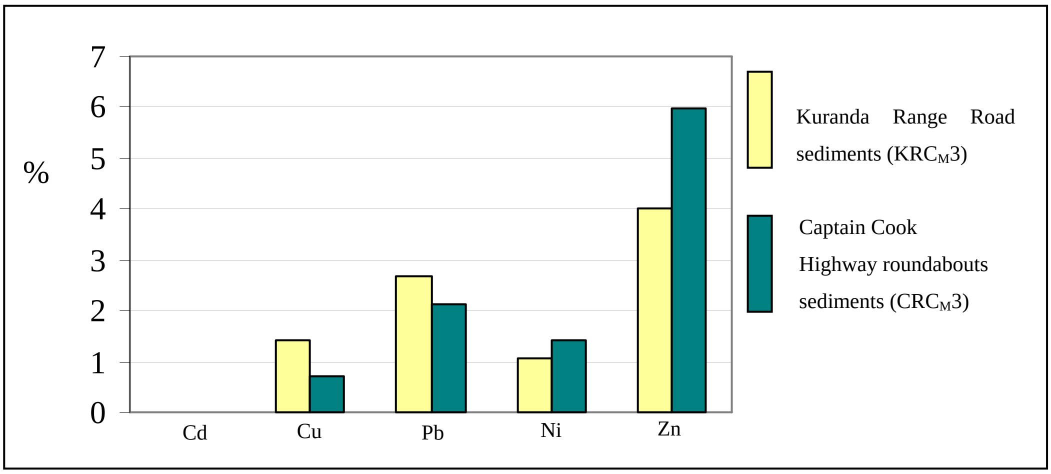


Figure 3-12: Calculated proportions of Cd, Cu, Pb, Ni and Zn in citrate-dithionite extracts. The partial extractions were performed on road sediments from the Kuranda Range Road and the Captain Cook Highway roundabouts (sampled August 2004). The individual metal concentrations have been averaged for all samples (n = 4 for the Kuranda Range Road and the Captain Cook Highway roundabouts) and calculated as a percentage of their respective total concentrations in the road sediment. Refer to Appendix A for sample ID for extracts and Appendix B for concentration data.

3.4 Discussion

3.4.1 Total heavy metal and PGE concentrations in road sediments

3.4.1.1 Comparison with other studies

Total metal concentrations detected in the road sediments in this study were compared with those reported for road sediments from other locations around the world (Table 3-5). Road sediment Zn, Pd and Pt values in this investigation were commensurate with and, in the case of Pd higher than, levels documented by other studies (Table 3-5). Median Cu concentrations in the road sediments from both the Kuranda Range Road and the Captain Cook Highway roundabouts were marginally lower than those values reported in sediments from more heavily trafficked roads (Table 3-5). Furthermore, Ni concentrations in sediments from this study were elevated relative to their respective values documented from road sediments by other studies (Table 3-5). Compared with the concentration range reported for Cd and Pb in road sediments in the literature, the levels of these metals in the road sediments analysed in this investigation were relatively low (Table 3-5).

Table 3-5: Comparison of total metal values in road sediments. All values in mg/kg.

	Mean concentration (mg/kg)	*Location/traffic density*	*Author*
Cd	2.78	Rural major road, Lancaster, UK	(Harrison et al. 1981)
	2.63	Highway, Merter, Istanbul, Turkey	(Sezgin et al. 2003)
	(median value) 0.19	Kuranda Range Road, 6 126 ADT	This study
	(median value) 0.21	Highway roundabouts, 30 000 ADT	This study
Cu	300	London, UK, 20 000 ADT	(Wang et al. 1998)
	296	Hong Kong, China, 45 000 ADT	(Wang et al. 1998)
	260	Parramatta Road, Sydney, Australia 73 177 ADT	(Birch and Scollen 2003)
	199	Rural major road, Lancaster, UK	(Harrison et al. 1981)
	189	Marion Street, Sydney, Australia, 22 618 ADT	(Birch and Scollen 2003)
	103	Highway, Merter, Istanbul, Turkey	(Sezgin et al. 2003)
	92	National Street, Sydney, Australia, <2 000 ADT	(Birch and Scollen 2003)
	73	Honolulu urban road, USA, 45 200 ADT	(Sutherland and Tolosa 2001)
	(median value) 42	Kuranda Range Road, 6 126 ADT	This study
	(median value) 57	Highway roundabouts, 30 000 ADT	This study
Pb	5779	Tunnel sediments, Caracas, Venezuela	(Fernandez and Galarraga 2001)
	2540	Rural major road, Lancaster, UK	(Harrison et al. 1981)
	1538	Parramatta Road, Sydney, Australia 73 177 ADT	(Birch and Scollen 2003)
	897	London, UK, 20 000 ADT	(Wang et al. 1998)
	737	Marion Street, Sydney, Australia, 22 618 ADT	(Birch and Scollen 2003)
	652	Hong Kong, China, 45 000 ADT	(Wang et al. 1998)
	470	National Street, Sydney, Australia, <2 000 ADT	(Birch and Scollen 2003)
	250	Honolulu urban road, USA, 45 200 ADT	(Sutherland and Tolosa 2001)
	281	Highway, Merter, Istanbul, Turkey	(Sezgin et al. 2003)
	(median value) 53	Kuranda Range Road, 6 126 ADT	This study
	(median value) 115	Highway roundabouts, 30 000 ADT	This study
Ni	36	Highway, Merter, Istanbul, Turkey	(Sezgin et al. 2003)
	34	Parramatta Road, Sydney, Australia, 73 177 ADT	(Birch and Scollen 2003)
	31	Marion Street, Sydney, Australia, 22 618 ADT	(Birch and Scollen 2003)
	24	Honolulu urban road, USA, 45 200 ADT	(Sutherland and Tolosa 2001)
	22	National Street, Sydney, Australia, <2 000 ADT	(Birch and Scollen 2003)
	(median value) 39	Kuranda Range Road, 6 126 ADT	This study
	(median value) 34	Highway roundabouts, 30 000 ADT	This study
Zn	2305	Hong Kong, China, 45 000 ADT	(Wang et al. 1998)
	1866	London, UK, 20 000 ADT	(Wang et al. 1998)
	1417	National Street, Sydney, Australia, <2 000 ADT	(Birch and Scollen 2003)
	1124	Highway, Merter, Istanbul, Turkey	(Sezgin et al. 2003)
	706	Parramatta Road, Sydney, Australia, 73 177 ADT	(Birch and Scollen 2003)
	578	Marion Street, Sydney, Australia, 22 618 ADT	(Birch and Scollen 2003)
	500	Honolulu urban road, USA, 45 200 ADT	(Sutherland and Tolosa 2001)
	458	Rural major road, Lancaster, UK	(Harrison et al. 1981)
	(median value) 852	Kuranda Range Road, 6 126 ADT	This study
	(median value) 619	Highway roundabouts, 30 000 ADT	This study
Pd	(median value) 0.060	Stuttgart, Germany, 120 000 ADT	(Schafer and Puchelt 1998)
	0.029	Heavily trafficked road, Karlsruhe, Germany	(Sures et al. 2002)
	(median value) 0.004	Karlsruhe, Germany	(Schafer and Puchelt 1998)
	0.004	Freiburg, Germany	(Schafer and Puchelt 1998)
	(median value) 0.035	Kuranda Range Road, 6 126 ADT	This study
	(median value) 0.099	Highway roundabouts, 30 000 ADT	This study
Pt	(median value) 0.280	Stuttgart, Germany, 120 000 ADT	(Schafer and Puchelt 1998)
	0.244	Heavily trafficked road, Karlsruhe, Germany	(Sures et al. 2002)
	0.148	Tunnel dust collected from Frankfurt, Germany	(Zereini et al. 1997)
	(median value) 0.060	Karlsruhe, Germany	(Schafer and Puchelt 1998)
	0.050	Freiburg, Germany	(Schafer and Puchelt 1998)
	0.033	Hawaii, USA, 45 000 ADT	(Sutherland 2003)
	(median value) 0.086	Kuranda Range Road, 6 126 ADT	This study
	(median value) 0.154	Highway roundabouts, 30 000 ADT	This study

3.4.1.2 Comparison with background values

Metal concentrations in the studied road sediments were compared with their levels in local background stream sediments (Table 3-2). This was done in order to provide an indication of the degree of metal enrichment in the road sediments. Median Pb, Zn, Pd and Pt concentrations were extremely enriched in the road sediment samples from both the Captain Cook Highway roundabouts (Pb 6.8x, Zn 9.7x, Pd 49.5x, Pt 82x) and the Kuranda Range Road (Pb 3.1x, Zn 13.4x, Pd 17.3x, Pt 46.5x) relative to background stream sediment values (Table 3-2). In comparison, enrichment factors for median Cd and Cu values in the road sediments were much lower (1 to 2x). In contrast to the other metals, median Ni concentrations in the background stream sediments were higher than median Ni values in the road sediments.

The observed enrichment of metals in the studied road sediments (Ni excepted) is attributed to sources within the immediate roadside environment. There are a multitude of anthropogenic and natural repositories of metals within roadside corridors. Cadmium, Cu, Pb, Ni, Zn, Pd and Pt are derived from the abrasion of several motor vehicle components including engines, brake pads, tyres and catalytic converters (Sansalone and Buchberger 1997; Zereini and Alt 2000). Moreover, metals are released from exhaust emissions and as well as the leakage of lubricants from vehicles (Al-Chalabi and Hawker 2000; Birch and Scollen 2003). In addition to motor vehicles, galvanised road infrastructure (e.g. sign posts and railings), bitumen and road paving materials are significant sources of anthropogenic metals (Van-Rooy 1991; Münch 1992; Smolders and Degryse 2002). Natural weathering of soil, rocks and biological material also contributes metals to sediments that accumulate on road surfaces (Sutherland et al. 2000).

In this study, the metal content of the local rocks were found to be comparatively low (Table 3-6). Consequently, the contribution of metals from local bedrock to the road sediments can be expected to be negligible.

Table 3-6: Metal concentrations (mg/kg) in rock types encountered in the project area.

Rock type	Cd	Cu	Pb	Ni	Zn	Pd	Pt
Granite (B1, n = 1)	0.03	26.8	19	18	79	0.008	0.0067
Metasiltstone (B2, n = 1)	0.04	66.5	20.1	20.5	86	0.003	0.0023
Hornfels (B3, n = 1)	0.02	18.6	8.9	16.8	74	0.003	0.0023

Moreover, SEM observations revealed the presence of various anthropogenic particles within the road sediments. A number of these particle types, namely the metallic shavings and tyre rubber shreds, are undoubtedly important contributors of metals to sediments. Consequently, in this study, various roadside anthropogenic sources (including abraded vehicle components and road infrastructure, vehicle emissions and road paving materials) likely account for the metal enrichment within the studied road sediments.

Metal contributions to the road sediments from other anthropogenic sources, away from the road environment, are likely to be inconsequential in this particular investigation. This is because there are no known metal-processing or mining land uses within proximity of the project area. Sutherland et al. (2000), who examined metal distributions in roadside corridors in Hawaii, similarly discounted industry and mining impacts in their research. In the absence of such confounding sources, they were able to propose automotive emissions and vehicle wear as the primary contributors to the elevated metal levels detected in their analysed road sediments.

3.4.1.3 Metal enrichment in local streams

In this study, Cd, Cu and Ni concentrations in the background stream sediments from Avondale Creek were commensurate with and above their respective levels in the studied road sediments (Table 3-1). The background stream sediment samples from both Streets Creek and Avondale Creek were collected from dense rainforest; several hundred metres upgradient of potential anthropogenic sources. Thus, anthropogenic contamination cannot account for this enrichment. Furthermore, base rock sample B2, taken from a metasiltstone outcrop at the upper reaches of Avondale Creek, did not indicate particularly high heavy metal or PGE concentrations (Table 3-6). Hence, alternative sources must be responsible for the Cd, Cu and Ni enrichment.

As discussed in Chapter 1, secondary minerals and organic materials have the capacity to adsorb and accumulate metals. Data produced by this study revealed that the organic carbon (C_{org}) content of the background stream sediments in Avondale Creek is extremely high (13 wt %). These stream sediments are derived from the surrounding soils of the Barron River catchment, which have been documented to be enriched in organic matter (C_{org} 3.5 wt %) compared with soil of other catchments in north Queensland (C_{org} <2 wt %) (Furnas 2003). Visual observation of the stream sediments from Avondale Creek confirmed the prevalence of an extremely fine, light brown substance, which appeared to consist of flocculated and colloidal organic matter. This abundant organic matter may have adsorbed mobile heavy metals, particularly Cd, Cu and Ni, thus resulting in the enrichment of these heavy metals. Therefore, Cd, Cu and Ni are likely enriched in the Avondale Creek sediment samples through natural environmental processes.

The other metals investigated in this study (Pb, Zn, Pd and Pt) were also elevated in the Avondale Creek stream sediments relative to the Streets Creek stream sediments, but not to the extent of Cd, Cu and Ni. Such metal distribution is likely due to organic matter’s preference for scavenging Cd, Cu and Ni over Pb and Zn (Parker and Rae 1998).

The natural enrichment of the metals Cd, Cu and Ni detected in this study highlights the fact that an assessment of anthropogenic contamination in the environment cannot be based solely on total metal concentrations. This is particularly true for cases where contamination is subtle. Moreover, studies in wet tropical locations need to consider the capacities of rainforest stream sediments to sequester metals through natural processes. Hence, caution must be exercised when using background values given by organic-rich stream sediments as a baseline to evaluate anthropogenic contamination processes in roadside environments.

3.4.2 Variations in heavy metal and PGE concentrations within the road sediments

Traffic density is the most widely reported variable influencing heavy metal and PGE concentrations in road sediments (Harrison et al. 1981; Schafer and Puchelt 1998; Viklander 1998; Birch and Scollen 2003). However, at a site-specific level there are a multitude of other factors including rainfall; road design; topography; and rate of atmospheric dust deposition, that result in wide variations in heavy metal and PGE concentrations in road sediments (Sutherland and Tolosa 2001; Thakur et al. 2004). These factors account for why, in certain cases, heavy metal and PGE concentrations are higher in road sediments on roads with lower traffic densities compared with more heavily-trafficked roads.

The following sections detail reasons for observed differences in heavy metal and PGE concentrations between sediments collected from the Kuranda Range Road, with an average daily traffic volume of 6,126 vehicles per day (Jones 2004) and the Captain Cook Highway roundabouts, with an average daily traffic volume of 30,000 vehicles per day (Jones 2004). Causes for temporal variations in metal concentrations within these sediments are also discussed with particular emphasis on trends in Pb concentrations. Such temporal trends will be evaluated considering that leaded petrol was completely phased out in Australia in 2002.

3.4.2.1 Effect of traffic density on metal concentrations in road sediments

Lead, Pd and Pt concentrations were consistently higher in sediment samples collected from the Captain Cook Highway roundabouts than the Kuranda Range Road (Table 3-5). The calculation of correlation coefficients using log-normalised data indicates some minor positive correlation between metal concentrations in road sediments and traffic density, as shown in Figure 3-13.

However, it should be noted that the correlations are not statistically significant at the $p<0.05$ or $p<0.01$ level.

The positive correlations between traffic density and Cu, Pb and Pt levels (R^2 values of 0.23, 0.13 and 0.13, respectively) in road sediments are likely due to the mechanisms by which these contaminants are released from motor vehicles. All of these metals are commonly liberated at continual rates by moving motor vehicles: Pb from exhaust emissions (Al-Chalabi and Hawker 2000); Cu primarily from engine wear (Viklander 1998; Birch and Scollen 2003); and Pd and Pt from high temperature reactions in catalytic converters (Higney et al. 2002). Slight variations in their level of release are induced by changes in motor vehicle behaviour; essentially their output is increased with acceleration and engine revving (Higney et al. 2002; Sezgin et al. 2003). Still, these variations are insufficient to negate the positive (albeit minor) correlations recorded between concentrations of these metals in road sediments and traffic density (Figure 3-13).

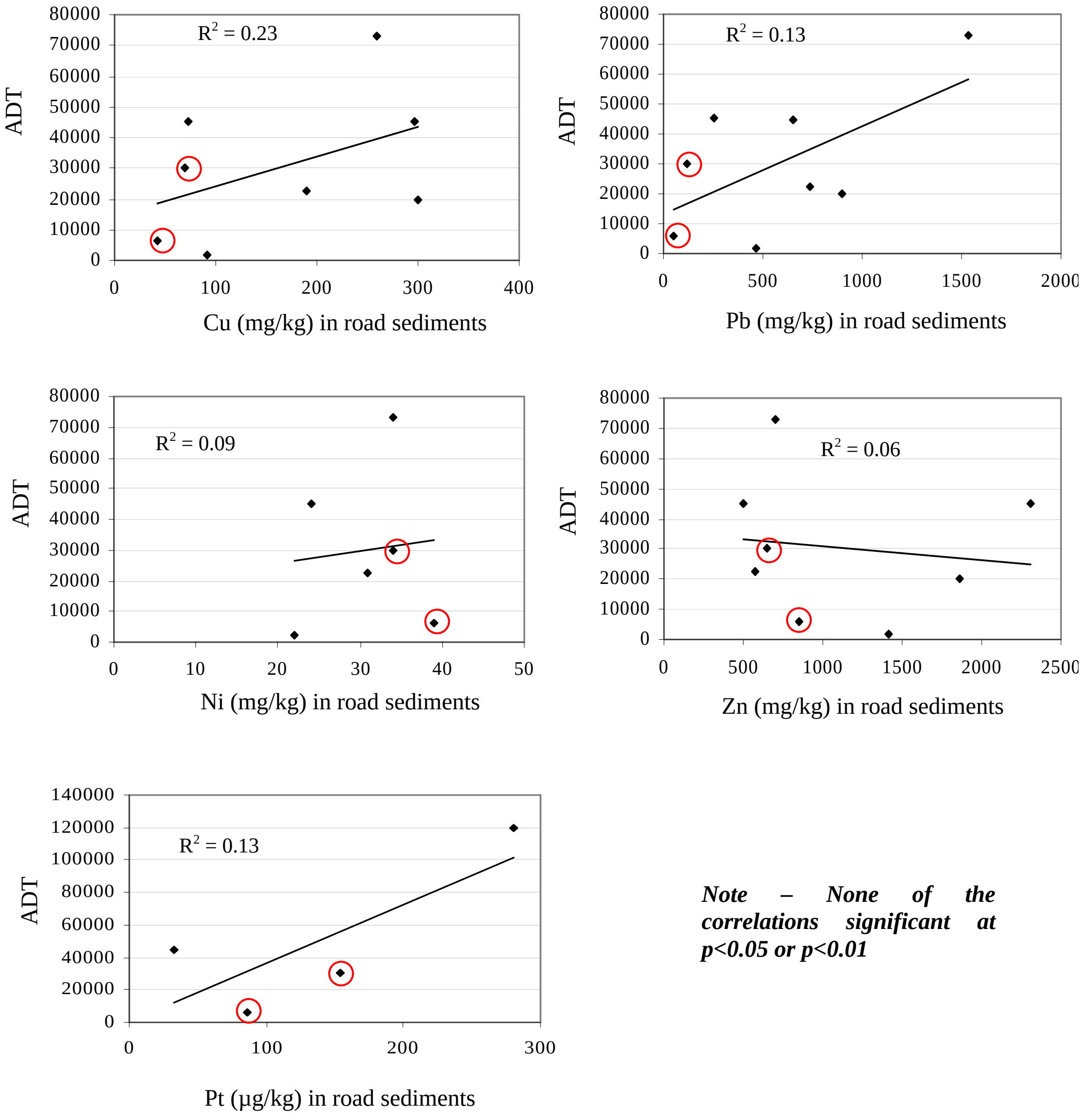
Conversely, Ni and Zn concentrations in road sediments do not exhibit strong trends with traffic density (Figure 3-13). The poor correlation between Ni concentrations in road sediments and traffic density ($R^2 = 0.09$) may be explained by the contribution of non-traffic-derived Ni in these sediments; namely from basalt gravel used in bitumen (Van-Rooy 1991).

By comparison, Zn is primarily derived from tyre wear (Fergusson and Kim 1991; Viklander 1998) as well as the abrasion of galvanised road structures (Smolders and Degryse 2002). Zinc concentrations do not show a strong dependence on traffic density, given that the rates of tyre abrasion are more related to other factors, including the physical properties of a road and its physiography.

Cadmium concentrations were only marginally higher in the Captain Cook Highway roundabout sediments than the Kuranda Range Road sediments (Table 3-5). It is likely that Cd exhibits a weak positive correlation with traffic density given that, like Cu, there are several key sources of Cd in the roadside environment (brake pads, engines and tyres).

It is plausible to suggest that Pd exhibits a similar relationship to traffic density as Pt, as these metals are emitted essentially from the same source (i.e. catalytic converters) in motor vehicles. Certainly, results from this study indicate that Pd concentrations were greater in the road sediments collected from the more heavily-trafficked Captain Cook Highway roundabouts than the Kuranda Range Road.

Finally, there is a lack of published data on Cd and Pd in roadside environments. Consequently, it is difficult to generate interpretations on the influence of traffic density on the concentrations of these metals in road sediments.



Note – None of the correlations significant at p<0.05 or p<0.01

Figure 3-13: Traffic density (ADT) and concentrations of Cu, Pb, Ni, Zn and Pt in road sediments (from Schafer and Puchelt 1998; Wang et al. 1998; Sutherland and Tolosa 2001; Birch and Scollen 2003; Sutherland 2003; and this study). Correlation coefficients were calculated using log-normalised data. Samples from this study are denoted by ○.

3.4.2.2 Control of road design and topography on road sediment Zn and Ni values

Zinc is frequently recorded in higher concentrations in sediments collected from roads with low traffic loads than those from heavily used roads (Table 3-5). This is further supported by the poor correlation between Zn concentrations in road sediments and traffic density (Figure 3-13). Hence, other influences (such as road design and physiography) appear to be far more significant in controlling Zn values in road sediments than traffic density. The importance of road physiography in controlling Zn accumulation in road sediments is clearly evident in the consistently high Zn concentrations in sediments from the winding Kuranda Range Road.

Zinc is largely discharged from vehicles as Zn-oxides from abrasion of rubber tyres (Smolders and Degryse 2002). Consequently, this metal is generally concentrated on road surfaces where corners are sharp and abrasion rates are high. Both the Kuranda Range Road and the Captain Cook Highway roundabouts possess sharp corners. Thus, road design alone cannot account for the greater Zn concentrations detected in sediments from the Kuranda Range Road. Topography can be viewed as a compounding factor influencing Zn output, with corners on steeper road curves (on the Kuranda Range Road) generating greater rates of abrasion of Zn-laden tyre surfaces than corners on flat road sections (the Captain Cook Highway roundabouts). This is due to the enhanced use of brakes on steep and windy road sections compared with flat road sections, which consequently results in greater rates of tyre/road surface friction.

Additionally, Ni is a commonly used metal in brake linings (Viklander 1998). Therefore, regular and rigorous use of brakes on the steep Kuranda Road may also partially account for the relatively high Ni concentrations detected in the sediments from this road.

3.4.2.3 Impact of rainfall on metal concentrations in road sediments

Rainfall has a significant effect on metal concentrations in road sediments since metals hosted by road sediments are subject to mobilisation by rainwater runoff. During rainfall, metals may be stripped from road sediments by dissolution in road runoff waters (Bourcier 1979). Furthermore, the fine-grained material of the sediments, which commonly hosts the greatest concentrations of metals (Viklander 1998), is readily physically mobilised by road runoff waters (Sansalone et al. 1998).

When comparing the study's data with those collated by Diprose (1999), the influence of rainfall in lowering heavy metal concentrations in road sediments is clearly observed. The sediments analysed in Diprose's study (1999) were collected in April 1999 from the Kuranda Range Road, immediately following the 'wet season' in Cairns. Conversely, the sediments examined in this study were acquired over a range of months, all within the north Queensland 'dry season' between August and November.

Table 3-7: Median heavy metal concentrations in road sediments collected from the Kuranda Range Road in this study, compared with mean concentrations from Diprose (1999).

	Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
This study (n = 30, median values)	0.185	42	53.3	39	852
Diprose (1999) (n = 5, mean values)	<1	23	39	12	65

The results in Table 3-7 indicate that heavy metal concentrations in road sediments are highest following an extended dry interval known as the 'antecedent dry day' (ADD) period (Han et al. 2005). Fergusson and Kim (1991) investigated the Pb concentrations in road sediments at a busy intersection in the city of Christchurch, New Zealand, over a number of years. Their study period encompassed several flooding and drought events (Fergusson and Kim 1991). Trends in road sediment Pb concentrations over the course of their study illustrate the impact of dry weather in increasing Pb concentrations (Figure 3-14). The figure also shows the influence of wet weather in reducing Pb concentrations in road sediments (Figure 3-14).

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Figure 3-14: Pb concentrations in road sediments with relation to weather conditions and the reduction in Pb in leaded petrol, at a busy intersection in Christchurch, NZ (from Fergusson and Kim 1991).

However, it should be noted that heavy metal concentrations do not always increase in road sediments over time following rainfall; at least not initially. This is demonstrated by work from Birch and Scollen (2003) who investigated Cu, Ni, Pb and Zn concentrations in road sediments in Sydney, Australia. They found no increase in metal concentrations in the road sediments during a period of 5 days following a rainfall event (Birch and Scollen 2003). Their finding indicates that a substantial period of time is required to permit the build-up of metal concentrations in road sediments following a rainfall event. However, prolonged episodes of drought (i.e. long ADD periods) between rainfall events eventually result in an increase in metal concentrations in road sediments (Fergusson and Kim 1991).

In wet-dry tropical locations, such as northern Australia, metal removal from road sediments by rainfall is an important process. The prolonged absence of rainfall facilitates the accumulation of metals within sediments that settle on road surfaces during the ‘dry season’. This investigation has shown that, in wet-dry tropical locations, maxima concentration data for road sediment-hosted metals are reported near the termination of the ‘dry season’.

3.4.2.4 Temporal trends in road sediment metal concentrations

Road sediments were collected in this study in October 2002, November 2003 and August 2004 in order to evaluate temporal changes in metal concentrations. Results of this investigation showed that Pb concentrations in road sediments from the Kuranda Range Road decreased marginally over the sampling period (October 2002 to August 2004) whereas a more pronounced decrease in Pb levels was observed in the road sediments from the Captain Cook Highway roundabouts (Figure 3-1).

It has been documented that the phasing out of leaded petrol causes a decrease in the Pb content of road sediments (Fergusson and Kim 1991). The study by Fergusson and Kim (1991) showed a decline in road sediment Pb levels at a major intersection in Christchurch, NZ, following a reduction in the Pb content of petrol in that country (Figure 3-14). A similar trend was also noted in road sediments collected from side roads to the intersection (Fergusson and Kim 1991).

However, Pb levels in roadside environments have not always been observed to decrease immediately following the reduction in the use of leaded petrol. A study by Birch and Scollen (2003) (Table 3-5) examined road sediment Pb levels in the inner Sydney area. They found Pb concentrations in Sydney were comparable to levels reported in highly-trafficked regions that continue to use leaded petrol, such as Venezuela, Ecuador and even Great Britain (Hewitt and Candy 1990; Fergusson and Kim 1991; Fernandez and Galarraga 2001; Bayford and Co Ltd 2004). Birch and Scollen’s (2003) study encompassed a period representing significant reduction in the use of leaded petrol in Australia. The elevated Pb concentrations recorded in their study may reflect a footprint of prolonged Pb accumulation from leaded petrol cars and industry in Sydney. In addition, results from a study conducted by Chiaradia et al. (1997) indicated that despite the phasing out of leaded petrol in Sydney in the 1990s, petrol still accounted for more than 90 % of the total Pb in the local atmosphere at that time. Their study highlights the persistence of Pb in the environment (Chiaradia et al. 1997).

By comparison, there has been a less extensive accumulation of Pb from vehicles in roadside environments in the Cairns area than larger cities in Australia (Table 3-5). This has likely resulted in the reduction in Pb road sediment concentrations observed in this study. Furthermore, the heavy ‘first flush’ downpours in tropical Australia are undoubtedly more rigorous in mobilising fine particulate and water-soluble Pb within road sediments than the less intensive rainfall experienced in southern, temperate locations within Australia.

Apart from a reduction in the use of leaded petrol in the Cairns region, variations in atmospheric conditions may also be responsible for the decrease in the Pb content in road sediments observed over the sampling period (October 2002 to August 2004). Cadmium, Cu, Ni and Zn are mobilised in association with larger abraded vehicle components, such as brake and engine shavings and tyre rubber particles (Sansalone et al. 1998; Viklander 1998), whereas Pb and the PGES are emitted from vehicles as fine dust particles (Rohbock 1981). This fine material is dispersed into the environment according to prevailing microclimatic conditions, including wind speed, wind direction and humidity (Gulson et al. 1981; Zereini and Alt 2000; Norra and Stuben 2004; Thakur et al. 2004). It can be seen in Figure 3-1 that those metals presumably transported as fine dusts (Pb, Pd and Pt) all displayed decreasing concentrations in the road sediments over time. It is hypothesised that these observed trends have been caused by fluctuations in the aforementioned microclimatic conditions, which are known to influence the rate of atmospheric dust precipitation (Chiaradia et al. 1997).

3.4.3 Particle-size distribution of Pb and PGEs in road sediments

Previous research has documented that heavy metals and PGEs are concentrated in the fine-grained fraction (<75 µm) of road sediments (Viklander 1998; Birch and Scollen 2003; Varrica et al. 2003). In general, concentrations of anthropogenic heavy metals in road sediments tend to decrease with increasing particle-size (Viklander 1998).

In this study, the individual metals exhibited variable concentrations in the different size fractions of road sediments. The varied distribution is influenced by the mechanisms controlling the accumulation of metals on the road surface. As discussed in Section 3.4.2.4, Pb and the PGEs (Pd and Pt) are largely deposited through the precipitation of atmospheric dust particles which are derived from vehicle emissions (Gulson et al. 1981; Chiaradia et al. 1997; Varrica et al. 2003). This explains why these metals are concentrated in the finer-grained particles of the road sediments from the Kuranda Range Road. However, Pd and Pt concentrations were greatest in the medium size particles (250 µm to 75 µm) in the sediments collected from the Captain Cook Highway roundabouts (Section 3.3.3). Moreover, the Pt concentrations in the 250 µm to 75 µm particle-size fraction of the Kuranda Range Road sediments were also considerable. These elevated PGE concentrations in the medium-size particles in the road sediments are most likely explained by clustering of finer particles with larger phases. Electrostatic attraction, possibly caused by the tyre rubber shreds in the road sediments, is proposed as a potential cause of metal clustering in this study. Clustering of metallic particles (including Pb) with larger mineral and anthropogenic particles in road sediments was documented by Varrica et al. (2003), although no mention was made in the study regarding possible mechanisms causing the clustering.

3.4.4 Particle-size distribution of Zn in road sediments

Zinc, which is derived primarily from tyre wear, was clearly concentrated in the medium-size particles in the Kuranda Range Road sediments (Figure 3-15). However, this trend was not evident in the Captain Cook Highway roundabout sediments, where Zn concentrations showed enrichment in the finer material (<106 µm) (Figure 3-15).

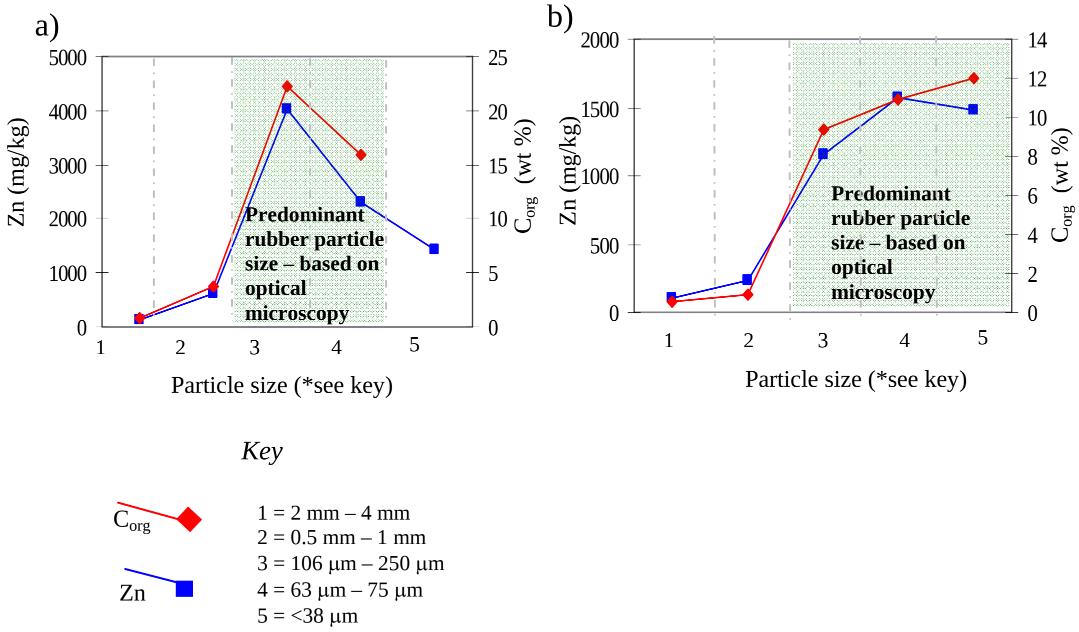

Figure 3-15: Relationship between Zn concentrations and C_{org} in road sediments from: a) the Kuranda Range Road; and b) the Captain Cook Highway roundabouts (November 2003).

Figure 3-15 displays the Zn and C_{org} concentrations in the various particle-size intervals of the road sediments analysed in this study. The C_{org} values were inferred to reflect the amount of tyre rubber particles in the samples. This stands to reason because tyre rubber is predominantly composed of carbon (Amari et al. 2000). Moreover, optical microscopy of the road sediments from the Captain Cook Highway roundabouts revealed that the <38 µm particle-size fraction in the sediments contained abundant tyre particles. It may be concluded that the Zn concentrations in the various particle-size fractions of the road sediments are dictated by the abundance of rubber particles.

The size of tyre rubber particles is likely influenced by road design. The Kuranda Range Road, which is steep and winding, probably causes greater abrasion rates of tyres and consequent shredding of larger rubber particles than the Captain Cook Highway roundabouts. Additionally, the predominant type of vehicle on a given road is another factor influencing the size of shredded tyre rubber particles. Tyre particles of trucks are commonly larger than those of cars by 15 µm to 20 µm (Smolders and Degryse 2002). Traffic data in Table 3-8 (see Appendix F for full traffic count details) indicate that the Kuranda Range Road accommodates a greater proportion of heavy vehicles, including trucks, than the

Captain Cook Highway (Queensland Department of Main Roads 2004f). This may explain the presence of larger tyre particles in the Kuranda Range Road sediments.

Table 3-8: Average daily proportions of light vehicles versus heavy vehicles on the Kuranda Range Road and the Captain Cook Highway. Proportions are expressed as percentages of the ADT (source, Queensland Department of Main Roads 2005).

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3.4.5 Particle-size distribution of Ni in road sediments

Of the metals examined in this investigation, Ni displayed the most complex particle-size distribution pattern in sediments from both the Kuranda Range Road and the Captain Cook Highway roundabouts. Nickel enrichment was observed in the coarse fraction of these sediments as well as in the fine material (Figures 3-3 and 3-4).

The elevated Ni concentrations in the coarse fraction of the sediments may be suggestive of clusters of smaller Ni-rich particles electrostatically attracted to the surfaces of the coarser particles. Clustering of fine metal-bearing particles in road sediments has been postulated by Varrica et al. (2003).

Alternatively, the high Ni content of the coarse proportion of the road sediments could be attributable to basalt-rich gravel and bitumen used to pave roads. Nickel contents of mafic rocks are known to be enriched compared with other crustal rock material (Faure 1991; Siegel 2002) and the use of basalt gravel in road aggregate is commonplace (Van-Rooy 1991). It should be noted that the study by Diprose (1999) revealed a Ni concentration of only 38 mg/kg for bitumen taken from the edge of the Kuranda Range Road. This low value may be due to a low Ni content in the matrix of the bitumen and a relatively low abundance of basalt gravel particles in the sampled aggregate.

The increasing Ni levels in the finer-grained sediments (<106 μm) analysed in this study (Figures 3-3 and 3-4) are commensurate with findings of Varrica et al. (2003). They recorded an abundance of Ni-rich particles in the <10 μm fraction of the road dusts analysed as part of their study. The primary sources of these particles are stainless steel shavings, presumably derived from engine and brake wear in motor vehicles (Varrica et al. 2003). In fact, Diprose's (1999) study revealed a Ni value of 582 mg/kg in brake pads, confirming the high Ni content of these vehicle components.

3.4.6 Heavy metal and PGE hosting by road sediments

An understanding of the solid-phase distribution of heavy metals and PGEs in road sediments is necessary to establish the potential aqueous mobility of these contaminants in road runoff waters that flush over road sediments during rainfall. The aqueous mobility of road sediment-hosted heavy metals is discussed in the next chapter.

The prominence of quartz, feldspar and muscovite in the road sediments examined in this study demonstrates that a considerable portion of these road sediments is composed of particles with low adsorptive capacities. These minerals do not influence the accumulation of metals in the road sediments. However, they do serve to dilute the heavy metal and PGE concentrations recorded within the coarse sediment fraction, as the particle size of these minerals is commonly in the 1000 µm to 2000 µm range (Table 3-4). In fact, it is the presence of secondary materials including oxide/hydroxides, carbonates, organic matter, clays, and abraded vehicle components (namely tyre rubber) that controls the distribution and reactivity of heavy metals and PGEs in the road sediments (Harrison et al. 1981; Fergusson and Kim 1991; Serrano-Belles and Leharne 1997; Wang et al. 1998; Li et al. 2001).

Several methods were conducted by this study to determine the solid-phase distribution of the metals in the road sediments. These included: a) sequential and partial extractions on the road sediments; and b) computational calculations performed on the geochemical data to evaluate the association of heavy metals and PGEs with organic matter as well as Al, Fe and Mn oxides, hydroxides and oxyhydroxides.

3.4.6.1 Sequential and partial extractions

The sequential extraction method used in this study, developed by Tessier et al. (1979), isolates solid-bound metals from five broad soil/sediment fractions into aqueous solutions. The solid phases include the exchangeable, carbonate, Fe-Mn oxide/hydroxide, organic and sulphide, and residual fraction (Tessier et al. 1979).

The applied sequential extraction procedure involved the addition of a progressively more acid and aggressive chemical reagent mixture to a mass of sediment. Theoretically, each of the respective five main phases targeted by the extraction process is increasingly stable. This is not always the case in practice, however, as exposed sulphides are highly unstable when exposed to oxygen (Caetano et al. 2003). Additionally, Fe-Mn oxides/hydroxides are unstable in strongly reducing conditions (Parker and Rae 1998).

In this study, the term ‘extractable’ is used to distinguish the exchangeable, carbonate, oxide/oxyhydroxide, organic/sulphide metal fractions from the residual metal phases in the road sediments. Moreover, water-soluble metals were investigated separate from the exchangeable metals in this study. In other investigations, water-soluble metals have been included as part of the exchangeable fraction (Harrison et al. 1981; Fergusson and Ryan 1984; Wang et al. 1998).

Results from other studies suggest that the exchangeable fraction (including water-soluble metals) generally only accommodates less than 10 % of the total metal content of road sediments (Table 3-9). The carbonate, oxide/oxyhydroxide and organic/sulphide fractions are commonly the most important host phases for heavy metals in road sediments (Table 3-9). In particular, the oxide/oxyhydroxide fraction has been shown to host elevated levels of heavy metals in other investigations (Table 3-9). The residual fraction is generally responsible for accommodating only negligible proportions of heavy metals hosted by road sediments. In fact, less than 20 % of heavy metals in road sediments collected from a number of locations around the world have been documented to be associated with the residual fraction (Table 3-9).

The results generated by the current study differed from those of other investigations in that much greater heavy metal concentrations were detected in the residual fraction (Table 3-9). Furthermore, the oxide/oxyhydroxide fraction was shown to host negligible amounts of heavy metals. In fact, Zn was the only heavy metal detected in this phase as determined by the sequential extraction.

Table 3-9: Calculated proportions (%) of Cd, Cu, Pb and Zn in road sediments (Harrison et al. 1981; Fergusson and Ryan 1984; Wang et al. 1998; and this study). The concentrations in all fractions have been calculated as a percentage of the total sediment metal content.

Harrison et al. (1981), London, Lancaster; <600 µm fraction

*	***E***	***C***	***Ox***	***Or***	***R***
Cd	20	38	28	8	6
Cu	7	18	4.5	58	12
Pb	1.5	43	38	7.5	10
Ni	-	-	-	-	-
Zn	2	44	43	7.5	4.5

Fergusson and Ryan (1984)
London, Halifax, New York, Christchurch, Kingston; particle-size fraction not specified

*	***E***	***C***	***Ox***	***Or***	***R***
Cd	17.7	31.4	38.3	7.8	4.7
Cu	1.9	34.1	44.2	7.1	11.2
Pb	1.3	8.6	11.3	53.2	25.6
Ni	-	-	-	-	-
Zn	3.4	30.2	50.8	9.1	6.6

Wang et al. (1998), Hong Kong; <125 µm fraction

*	***E***	***C***	***Ox***	***Or***	***R***
Cd	-	-	-	-	-
Cu	2	1	18	71	8
Pb	4	1	75	11	9
Ni	-	-	-	-	-
Zn	0	0	90	7	3

This study

*	***W***	***E***	***C***	***Ox***	***Or***	***R***
Cd	1.2	10.6	21	0	33	34.7
Cu	1.1	0.8	4	0	13	81.5
Pb	0.3	0	23	0	0	77
Ni	0.8	0.7	1.5	0	2	95.1
Zn	1	3	28	10	0	58

* *W = water-soluble fraction, E = exchangeable fraction, C = carbonate-fraction, Ox = oxide/oxyhydroxide fraction, Or = organic/sulphide fraction, R = residual fraction*

Moreover, results from the citrate-dithionite tests confirmed the low concentrations of metals in the oxide/oxyhydroxide fraction of the road sediments. This was the case for sediments from the Kuranda Range Road and the Captain Cook Highway roundabouts (Figure 3-12).

The comparatively low metal concentrations in the oxide/oxyhydroxide fraction could be an artefact of the applied sequential and partial extraction techniques. This is plausible, considering that there are numerous well-documented problems associated with extraction procedures (i.e. loss of sample between steps, variations in the buffering capacity of soil and sediments, and the non-selectivity of reagents coupled with metal readsorption). It is necessary to elaborate on these flaws in order to elucidate which problems are likely to have had the greatest influence on the results of the sequential extraction performed in this study.

To begin with, loss of sample material between the various steps of extraction procedures represents a significant problem. A vast number of extractions reported in the literature (e.g. Harrison et al. 1981, Lee et al. 1997, Wang et al. 1998, Turner et al. 2001) are based on the method developed by Tessier et al. (1979) who prescribed the addition of various extraction reagents to a single 1 g aliquot of sediment. However, loss of sample material in this study was overcome by using separate sediment aliquots for the various stages of the extraction sequence.

In addition to sample material loss, Serrano-Belles and Leharne (1997) uncovered problems in sequential extractions relating to variations in the buffering capacities of soils and sediments. Their work showed that the presence of high carbonate levels in road dusts strongly buffered against Pb liberation under weak acid leaches. This finding is important because the carbonate destruction step in many sequential extractions involves the use of a weak acid, most commonly Na-acetate adjusted to pH 5 with acetic acid (Tessier et al. 1979).

The C_{carb} content of the road sediments examined in this study was approximately 3 wt %; much lower than the C_{carb} values (11 wt %) in the road dusts analysed by Serrano-Belles and Leharne (1997). Furthermore, the sequential extraction revealed a high proportion of Pb in the carbonate fraction (23 %). Consequently, it is unlikely that the buffering capacity of the road sediments examined in this study had any substantial influence on the results of the sequential extraction.

In contrast, the problems of non-selectivity of reagents coupled with metal readsorption may have seriously impacted on the results of extractions performed in this research. Non-selectivity of reagents was encountered by Turner et al. (2001) who examined metal partitioning in roadside topsoils, Cincinnati, USA. Their extraction technique indicated (falsely) that Pb and Zn in their studied soil samples were primarily bound in residual silicate phases. Only a small proportion of these two metals were extracted by the solution used to target the organic phases in the soils (Turner et al. 2001). However, correlation analysis showed that both Pb and Zn were strongly associated with the organic carbon fraction (Turner et al. 2001). Additional tests performed on the soil samples indicated that significant amounts of organic carbon remained following the organic phase extraction step of the sequence (Turner et al. 2001). It was clear that the extraction step was non-selective in digesting the entire organic fraction. Consequently, it was determined that large proportions of Pb and Zn in the soil samples were associated with relatively insoluble organic compounds, which were not easily extracted using common sequential techniques (Turner et al. 2001). As a result, Pb and Zn bound in these insoluble organic phases, were removed in the last step of the sequence, which targeted residual solid fractions.

When extraction reagents are non-selective, metals dissolved in a certain step in extraction sequences can be promptly readsorbed by remaining stable fractions in sediments or soils. As a result, the metal contribution to the phases targeted by the following steps is overestimated. For example, Harrison et al. (1981), who performed a sequential extraction on roadside topsoils, found that a substantial proportion of Pb detected in the organic/sulphide phase was associated with the carbonate and Fe-Mn oxide phases that had not been previously removed. This resulted in an overestimation of Pb attributed to the organic fraction.

In this study, non-selectivity of reagents coupled with metal readsorption may have resulted in the relatively low metal values detected in the oxide/oxyhydroxide and organic/sulphide fractions. Such processes would have led to the exceptionally high metal levels recorded in the residual fraction of the road sediments.

Other problems associated with extraction procedures revolve around variations in the physical composition of sediments and soils, and these problems cannot be discounted in this study. Carbonates, clays and oxide/oxyhydroxides, as well as organic compounds, are bound together in soils and sediments as aggregate substances (Parker and Rae 1998). The coating of clay minerals with amorphous oxides/hydroxides; the binding of charged humic compounds to oxides/hydroxides; and the precipitation of carbonate minerals on clays and oxides/hydroxides, are examples of processes that have been documented to occur in soils and sediments, depending on local chemical conditions (Parker and Rae 1998). Common sequential extraction procedures do not account for such interactions between solid phases in sediments and soils and, as such, may not effectively breakdown complex bonds.

Despite the recorded problems associated with sequential extraction techniques, information on metal distributions provided by these procedures is still useful in assessing the mobilisation potential of metals from contaminated sediments. However, the aforementioned inadequacies of sequential and partial extractions demonstrates that additional analytical techniques should be pursued to validate the accuracy of results given by the extractions, especially when examining road sediments. After all, it should be noted that Tessier's et al. (1979) method and the citrate-dithionite partial extraction tests were not designed for 'artificial sediment' containing tyre rubber shreds.

3.4.6.2 Correlations

Overall, heavy metal concentrations in the road sediments were poorly correlated with Al, Fe and Mn levels (Table 3-10). These weak correlations provide further evidence that oxide/oxyhydroxide phases host minimal metal concentrations in these road sediments. Certain metals, notably Pt, were strongly negatively correlated with Al, Fe and Mn concentrations in road sediments. In fact, Pb, Pd and Pt were all significantly inversely correlated with Al (Table 3-10). In contrast, Ni concentrations were significantly positively correlated with Fe levels ($p<0.01$ level). Thus, this relationship provides evidence for Ni hosting by

Fe-oxyhydroxides within the road sediments, despite the paucity of oxide/oxyhydroxide Ni determined by the sequential and partial extractions.

Concentrations of Cd, Cu, Pb, Ni, Zn and Pt as well as C_{org} levels were determined in the various grain size fractions of two homogenised sediment samples collected from the Kuranda Range Road and the Captain Cook Highway roundabouts in August 2004 (KRC_M3 and CRC_M3, respectively). The heavy metal concentrations showed strong correlations with the C_{org} levels in the various size fractions. Correlation coefficients (R^2 values) between log-normalised C_{org} values and log-normalised metal concentrations were: + 0.88 for Cd; + 0.78 for Cu; + 0.89 for Pb; + 0.98 for Zn; and + 0.74 for Pt. Only Ni displayed a negative correlation with C_{org} levels ($R^2 = - 0.12$). Correlations between Cd, Cu, Pb, Zn and C_{org} were all significant at the $p<0.01$ level.

Organic carbon has been demonstrated to be closely correlated with heavy metal concentrations in the previously described study by Turner et al. (2001) (Section 3.4.6.1). Their investigation focused on roadside soils. However, as was the case in this study, they found only low concentrations of these metals were extracted from the organic fraction by sequential extraction, despite strong correlations between heavy metals and C_{org}. The association of heavy metals with tyre rubber particles in the roadside soils may well have accounted for their documented results.

Overall, tyre rubber appears to be an important host for metals within the studied road sediments. The presence of Zn in tyre particles was evidenced by SEM-EDS investigations. Moreover, metal values and C_{org} levels were significantly positively correlated in the road sediments (Table 3-10), providing further support that tyre rubber particles represent critical host sites for metals. However, the sequential extraction technique revealed low metal contents in the organic-sulphide fraction. This indicates that the bonds between the rubber particles and the metals are difficult to break with mild to weak acids applied during the sequential extraction. Alternatively, these tyre rubber particles may be efficient scavengers of heavy metals released by the extraction agents and sequester metals quite rapidly once they are released into the solution. Both of these possibilities highlight the problems relating to non-selectivity of reagents and metal readsorption that are inherent in extraction procedures. The limitations of sequential extractions must be considered during any study because, for a given environment, the extractability of an element from solid phases in soil and sediments will depend on the physical, chemical and biological conditions of that particular setting (Siegel 2002).

In this work, it was evident that the reagents used in the sequential and partial extractions were ineffective in digesting the tyre rubber particles in the road sediments. This study has clear implications for future investigations into metal partitioning in road sediments. The research has demonstrated that results from extraction procedures must be supplemented by additional data (such as correlation analyses between metal and C_{org} values and SEM-EDS analyses) in any study examining the solid-phase hosting of metals in sediments or soils.

Table 3-10: Correlation coefficient matrix for log-normalised metal concentrations and log-normalised C_{org} values in road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts. For metal vs. metal correlations, n = 11. For metal vs. C_{org} correlations n = 9.

Cd	-								
Cu	+ 0.03	-							
Pb	+ 0.06	+ 0.02	-						
Ni	+ 0.06	+ 0.07	- 0.34	-					
Zn	+ 0.50	+ 0.01	0	+ 0.28	-				
Pd	+ 0.12	+ 0.21	+ 0.01	0	+ 0.06	-			
Pt	+ 0.11	+ 0.27	+ 0.03	0	+ 0.04	+0.78	-		
Al	- 0.11	- 0.11	- 0.35	+ 0.12	- 0.03	-0.51	-0.71	-	
Fe	0	- 0.07	- 0.48	+ 0.67	+ 0.10	-0.03	-0.10	+0.42	-
Mn	+ 0.02	+ 0.31	- 0.21	+ 0.42	+ 0.08	+0.03	0	+0.20	+0.42
C_{org}	+ 0.88	+ 0.78	+ 0.89	- 0.12	+ 0.98	-	+ 0.74	-	-
	Cd	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**	**Al**	**Fe**

Notes: Type of correlation is indicated by +/- symbol
Correlation is significant at the $p<0.05$ level
Correlation is significant at the $p<0.01$ level

3.5 Conclusions

Road sediments were found to commonly occur as loose, fine to coarse-grained particles in gutters along the Kuranda Range Road and Captain Cook Highway roundabouts. Solid phases included minerals (quartz, K-feldspar, albite and muscovite) of the surrounding soils and rocks as well as anthropogenic materials (tyre particles, reflective glass beads, paint flecks and metallic shavings).

The road sediments exhibited variable total metal values, including major concentrations of Zn (>1000 mg/kg), minor levels of Cu, Pb and Ni (ca. 10 to 1000 mg/kg) and trace amounts of Cd, Pd and Pt (<1 mg/kg). Moreover, determination of the metal distributions in these sediments showed that Cd, Cu, Pb, Pd and Pt were concentrated in the fine-grained fraction of the sediments (<75 μm). By comparison, Zn concentrations were highest in the medium to fine-grained material (<250 μm). Nickel displayed a biomodal distribution as it was enriched in the coarse-grained (>1 mm) as well as the fine-grained (<75 μm) sediments.

Extraction analyses indicated that Cd was predominantly hosted by carbonate, organic/sulphide and residual sites. Copper, Pb, Ni and Zn were primarily associated with the residual fraction. Significant positive correlation coefficients existed between C_{org} levels and Cd, Cu, Pb, Zn and Pt values in the studied road sediments.

Comparisons between this study and other investigations revealed relatively high total concentrations of Zn, Pd and Pt in the road sediments collected in this project. Zinc values were higher in the road sediments collected from the Kuranda Range Road than the more heavily trafficked Captain Cook Highway roundabouts (Table 3-5). This indicates that traffic density is not the sole factor in determining the release rate of traffic-derived Zn into roadside environments. Road design, physiography and weather patterns are other possible influences on metal concentrations in road sediments.

The road sediments analysed in this study were enriched in all metals (maximum enrichment factors: Cd 1.8x, Cu 1.5x, Pb 6.8x, Zn 17.3x, Pd 49.5x, Pt 82x), with the exception of Ni, relative to local background stream sediments. Moreover, sediments from one of the local background streams (Avondale Creek) showed an enrichment of Cd, Cu and Ni. This is likely due to accumulation of these metals by the abundant organic matter recorded in this stream.

The particle-size distribution of heavy metals and PGEs in the sediments collected in this study shows that these metals are not exclusively restricted to the most fine-grained material. The particle-size distribution of tyre rubber shreds appears to exert the greatest influence on metal distribution in the sediments, particularly for Zn.

Results of a sequential extraction performed on road sediments collected from the Kuranda Range Road in August 2004 suggest that Cd, Cu, Pb, Ni and Zn were primarily hosted by residual sites. The metals hosted by this fraction were not easily extracted by weakly acidic to mildly acidic reagents. This finding differed from those of other studies, because the oxide/oxyhydroxide fraction has been widely documented as a significant host phase for heavy metals in road sediments in Australia and overseas. However, results of a partial citrate-dithionite extraction performed on sediments collected from the Kuranda Range Road and the Captain Cook Highway roundabouts confirmed that the oxide/oxyhydroxide fraction hosted only minimal heavy metal concentrations. This finding was further supported by the weak correlations recorded between the heavy metals (Ni excepted) and Al, Fe and Mn in the road sediments.

Significant ($p<0.01$) positive correlations recorded between the Cd, Cu, Pb and Zn and C_{org} suggested that tyre rubber particles are important hosts for metals in road sediments. This was further supported, in the case of Zn at least, by the presence of Zn in tyre rubber particles as shown by SEM/EDS observations. The tyre rubber particles are likely efficient adsorbers of heavy metals which are not liberated by weak to mild acid reagents. The levels of tyre rubber observed in the road sediments in this study were exceptionally high as indicated by C_{org} values.

The research has clearly demonstrated that extraction procedures must be complemented by additional analyses, such as correlations between metal, oxide and C_{org} values in any study examining the solid-phase hosting of metals in sediments or soils. The study has shown that metals are closely associated with tyre rubber shreds in road sediments. It is therefore pertinent to investigate the metals' mobility in rainwater runoff during the 'wet season' in the tropics. Of particular relevance is the effect of chemical conditions of these waters on metal mobility in roadside environments.

Chapter 4 Metal mobility in road runoff waters

4.1 Introduction

Heavy metals that are hosted by road sediments are mobilised from the road surface and flushed into the stormwater drainage network (McRobert and Sheridan 2001). Stormwater from roads ultimately delivers the most labile fraction of metal contaminants to soils, streams and potentially oceans (Sansalone and Buchberger 1997; Rose et al. 2001). Consequently, metals transported by road runoff waters may become bioavailable to organisms living in environments that receive these waters.

Studies focusing on storm and road runoff waters often simply separate aqueous metal concentrations into dissolved (<0.45 µm) and total (>0.45 µm) fractions (Rose et al. 2001). However, the speciation of metals in these waters is often significantly more complicated. It can be argued that there are essentially four main types of metal-phases in runoff waters, all of which can be readily transported from road edges over soils and into streams. These include: a) solid fractions which may be physically mobilised by flowing water (Sansalone et al. 1998); b) colloidal phases which remain suspended in solution due to electrostatic repulsion, even under conditions of zero flow (Parker and Rae 1998); c) metal-complexes which can vary greatly in size as well as adsorption/desorption potential (Parker and Rae 1998); and d) dissolved species which include hydrolysed and cationic metal species (Parker and Rae 1998; Rose et al. 2001).

Large solid particles are commonly only transported very short distances from road edges owing to their dependence on strong flows to keep them in motion (Sansalone et al. 1998). By comparison, solid particles which are <75 µm can be transported several kilometres by suspension before they settle as stream, lake or ocean bed sediments (Parker and Rae 1998).

Colloidal, complexed and dissolved metal species are documented as having the greatest environmental significance (Parker and Rae 1998). This is due to the fact that these are the most labile and mobile fractions in road runoff waters. Moreover, these species are generally highly reactive in aqueous solutions under minor changes in chemical and physical conditions (e.g. pH, Eh, temperature) (Parker and Rae 1998).

In practice, it is extremely difficult to distinguish between colloidal, complexed and dissolved metal species in waters due to the extremely variable sizes of colloids and complexes (from nanometres to 1 µm) (Parker and Rae 1998). Thus, the common perception that filtering of water samples through 0.45 µm diameter apertures leaves only dissolved metal species in solution (Sansalone and Buchberger 1997; Rose et al. 2001) is not entirely accurate, as colloids and complexes have been documented to pass through filter diameters of this size (Siegel 2002). Despite this, there is common agreement that the <0.45 µm filtrate (referred to as the 'dissolved' fraction throughout the remainder of this document) yields the most labile and, therefore, most readily bioavailable fraction of metal contaminants in water samples (Dierkes and Geiger 1999).

There have been many studies examining metal phases in road runoff waters within temperate locations around the world. Previous research has demonstrated that suspended particles are important host sites for Pb, Cu and Zn in road runoff waters. For example, Mangani et al. (2005) found that suspended particulates contributed the greatest Cu, Pb and Zn concentrations in highway runoff waters in central Italy. Maximum particulate Cu, Pb and Zn levels were approximately 7x, 80x and 25x higher than their corresponding dissolved concentrations (as determined by the 0.45 µm filtrate) (Mangani et al. 2005). Similarly, Backstrom et al. (2003) determined that particulate metal concentrations were higher than dissolved metal levels in road runoff waters collected from a number of roads in Sweden. In their study, maximum particulate Pb and Zn concentrations in the runoff waters were 6x and 2x higher than their dissolved levels, respectively (Backstrom et al. 2003). In agreement with Mangani et al. (2005) and Backstrom et al. (2003), Muhammad et al. (2004) note that over 50 % of pollutants in road runoff waters are carried in suspension. In addition, Starzec et al. (2005) claim that 40 to 70 % of many metals are associated with particulates in road and highway runoff waters. Bourcier (1979) also showed that Pb and Zn were primarily present as particulate phases in road runoff waters of a highway in Washington State, USA. By comparison, a limited number of studies have reported certain metals, namely Cd, Cu and Zn, to be mainly present as dissolved species in road runoff waters (i.e. as determined by the <0.45 µm filtrate) (Sansalone and Buchberger 1997; Dierkes and Geiger 1999; Rose et al. 2001).

In comparison to all other metals, there has been scant research documenting Ni distributions in road runoff waters. A study by Rose et al. (2001) determined no significant enrichment of Ni in the 0.45 µm filtrate of road runoff waters compared with background stream waters in Atlanta, USA. Furthermore, a study by Drapper et al. (1997) revealed relatively low total Ni concentrations (mean value of 2 µg/L) in road runoff waters in south-east Queensland, Australia (Drapper et al. 1997).

Few investigations have examined seasonal trends in aqueous metal concentrations in road runoff waters. For example, a study by Sansalone and Buchberger (1997), conducted in a wet-temperate location in the USA, showed that Cd, Cu and Zn concentrations are markedly highest in the earliest runoff water volumes of a rainfall event. This phenomenon is described as the ‘first flush’ effect which is defined as “the delivery of a disproportionately large load of constituents during the early stages of the runoff hydrograph” (Sansalone and Buchberger 1997). In the investigation conducted by Sansalone and Buchberger (1997) it was noted that Pb concentrations demonstrated a weak ‘first flush’ effect. Drapper et al. (2000) also examined ‘first flush’ concentrations of Cu, Pb and Zn in road runoff waters in south east Queensland, Australia. Their study documented elevated total levels of these metals within ‘first flush’ waters. Moreover, the maximum concentrations of these metals in the studied road runoff waters were within the range common of more heavily trafficked regions in the world (Drapper et al. 2000).

Despite the extensive research by the aforementioned investigations, there has been no examination of metal mobility in road runoff waters within wet-dry tropical locations. Furthermore, there have been no water-leaching studies performed on road sediments to explore trends in metal dissolution from these sediments. Additionally, the aqueous mobility of road sediment-hosted metals in ponded water bodies remains unexamined. This is despite the fact that research into the effects of ponding on the aqueous mobility of heavy metals is important because road sediments are not necessarily continually flushed from road pavements and gutters by runoff waters. During low-intensity rainfall events, road runoff waters stagnate or pond with sediments in gutters. Thus, metal contaminants mobilised from road sediments within these ponded water bodies may seep over soils or into streams.

This chapter investigates the aqueous mobility of road-sediment hosted heavy metals in road runoff waters. Specifically, the objectives are: a) to examine the unfiltered and filtered (<0.45 μm) fractions of Cd, Cu, Pb, Ni and Zn in road runoff waters on the Kuranda Range Road and the Captain Cook Highway roundabouts; and b) to examine the effects of leaching and ponding on the aqueous mobility of road sediment-hosted heavy metals through laboratory experiments.

4.2 Methods of analysis

Rainwater samples collected from Yorkeys Knob, Cairns (refer to Appendix A for details) as well as road runoff water samples taken from the Kuranda Range Road and the Captain Cook Highway roundabouts during rainfall events in January and November 2004, were analysed for their pH and EC values at JCU, Cairns (Chapter 2 – Section 2.5.1). Additionally, the road runoff water samples collected in January and November 2004, as well as road runoff waters acquired in February 2003, were split into filtered (<0.45 μm) and unfiltered samples. The samples were analysed for their Cd, Cu, Pb, Ni and Zn concentrations at the AAC, Townsville (Chapter 2 – Section 2.5.2).

Further to the above, laboratory leaching and ponding experiments were performed on road sediments taken from the project area (Chapter 2 – Section 2.4.6). In the column leach tests, successive volumes of distilled water were poured through a plastic column containing road sediments (Chapter 2 – Section 2.4.6.1). The pond experiments were performed over a period of 3 months and samples were decanted at regular intervals (Chapter 2 – Section 2.4.6.2). All leachates and decant waters were split into filtered (<0.45 μm) and unfiltered samples. pH, Eh and dissolved oxygen (DO) values were measured in the unfiltered leachates at JCU, Cairns (Chapter 2 – Section 2.4.6.1 and 2.4.6.2). Moreover, portions of filtered and unfiltered leachates were analysed for their Cd, Cu, Pb, Ni and Zn concentrations at the AAC, Townsville (Chapter 2 – Section 2.4.7.2).

Finally, laboratory experiments were performed on tyre rubber shreds which were ponded with distilled water (Chapter 2 – Section 2.6). The shreds were ponded for a period of 1 month and samples were split into filtered and unfiltered portions. pH and Eh values were measured in the unfiltered portions, while the filtered waters were analysed for their Cd, Cu, Pb, Ni and Zn values at the AAC, Townsville (Chapter 2 – Section 2.6).

4.3 Results

4.3.1 Chemical parameters of background rainwater

Seven rainwater samples were collected from Yorkeys Knob, Cairns (see Figure 2-22 for location and Appendix A for sample ID details). The samples were analysed for their pH and electrical conductivity (EC) values, and the results are presented in Table 4-1.

The pH values of the samples indicated a slightly acidic nature for rainwater in the region. Furthermore, the mean pH value of the samples (Table 4-1) was in the average range for rainwater pH levels, worldwide (Faure 1991). The EC values for the rainwater samples (Table 4-1) were generally very low (pure rainwater should have an EC value close to 0 µSm/cm; Faure 1991).

Table 4-1: pH and EC values for rainwater samples. Refer to Chapter 2 – Section 2.5 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

	Mean value (n = 7)	Range
pH	5.86	5.43 – 6.15
EC (µSm/cm)	51.9	4 – 93

4.3.2 Chemical parameters of road runoff waters

Road runoff water samples were collected from the Kuranda Range Road and the Captain Cook Highway roundabouts in January 2004 and November 2004. The waters were analysed for their pH and EC values and the results are shown in Table 4-2. The pH values of road runoff water samples were consistently higher than those recorded in the pure rainwater samples (Table 4-1). Similar mean pH values were evident in the January 2004 and November 2004 road runoff water samples (Table 4-2). EC values were higher in the samples collected in November 2004 than in the waters obtained in January 2004 (Table 4-2). Moreover, EC values in the January 2004 road runoff water samples were in the range common for pure rainwater, whereas EC values recorded in November 2004 samples were well above average rainwater values (Table 4-2).

Table 4-2: pH and EC values in the studied road runoff water samples. Refer to Chapter 2 – Section 2.5 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

		Kuranda Range Road		***Captain Cook Highway roundabouts***	
		Mean	Range	Mean	Range
pH	*January 2004*	6.74 (n = 4)	6.32 - 7.03	6.62 (n = 4)	6.56 - 6.71
	November 2004	6.92 (n = 9)	5.60 - 9.02	6.45 (n = 4)	5.92 - 6.98
EC (µS/cm)	*January 2004*	23.85 (n = 4)	9.4 - 35	16.75 (n = 4)	13 - 20
	November 2004	841.2 (n = 9)	76 - 2074	288.5 (n = 4)	236 - 422

4.3.3 Aqueous metal concentrations in road runoff waters

The road runoff water samples taken from the Kuranda Range Road and the Captain Cook Highway roundabouts in January 2004 and November 2004 were separated into filtered (<0.45 µm) and unfiltered portions. Additionally, road runoff waters acquired from these roads in February 2003 were filtered (<0.45 µm). Aqueous Cd, Cu, Pb, Ni and Zn concentrations were measured in all of these road runoff water samples (filtered and unfiltered) and the data are presented in Tables 4-3 and 4-4.

The individual road runoff water samples yielded varying metal concentrations (Table 4-3, 4-4). Zinc was detected in the highest levels (10 to >1000 μg/L), whereas Cd values were consistently below detection (0.05 µg/L) in most samples. Median heavy metal concentrations were highest in the samples collected in November 2004 (Table 4-3, 4-4).

The data in Tables 4-3 and 4-4 indicate that median Cu, Ni and Zn concentrations in the filtered road runoff water samples were nearly as high as their total levels in the unfiltered samples. In contrast, Pb concentrations in filtered samples were much lower than the respective total aqueous Pb levels, especially in the road runoff waters collected from the Captain Cook Highway roundabouts (Table 4-3, 4-4).

Copper, Pb, Ni and Zn values in the road runoff water samples were frequently above local background stream levels (Table 4-3, 4-4). In a number of these stream water samples, and the road runoff water samples, metal values in filtered waters were higher than their corresponding levels in unfiltered waters. In such cases it was inferred that most of the metal was dissolved and that poor analytical accuracy led to slightly higher dissolved metal values than total concentrations. Additionally, contamination from the filtering process may have affected the results, although this is expected to be minor as all filtering equipment was rinsed in dilute HCl prior to use.

Metal concentrations in the road runoff water samples were compared with the most stringent threshold levels (i.e. the 99 % Protection Level) stipulated by the Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines for the Protection of Freshwater Ecosystems (Australian Department of Environment and Heritage 2000b). Most metals were present above ANZECC (2000) threshold values in filtered or unfiltered road runoff waters collected from the Kuranda Range Road (Table 4-3). Additionally, Cu and Zn values exceeded these ANZECC Guidelines (2000) in both filtered and unfiltered waters (Table 4-3). By comparison, Cd, Cu, Pb and Zn concentrations breached the ANZECC Guidelines (2000) in at least one sample taken from the Captain Cook Highway roundabouts over the sampling intervals. Only Ni was below the ANZECC Guidelines (2000) in all samples (Table 4-4).

Two stream water samples from Streets Creek (upstream of all roads) were also split into filtered and unfiltered portions and analysed for their metal concentrations (Table 4-3, 4-4). It can be seen that Zn values in these waters were in excess of the adopted ANZECC Guidelines (2000) for high ecosystems of high conservation value (i.e. the 99% Protection Level for Freshwaters). Hence, these guideline values should be considered in conjunction with background stream water metal concentrations when assessing contamination within local catchments.

Table 4-3: Heavy metal chemistry of road runoff waters, Kuranda Range Road (n = 5, February 2003; n = 4, January 2004; n = 9, November 2004). ANZECC Guidelines (2000) for the Protection of Freshwater Ecosystems (99 % Protection Level) are also included. Refer to Chapter 2 – Section 2.5 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

		February 2003		***January 2004***		***November 2004***		***Background stream water* concentrations (µg/L)***	***ANZECC, 2000 (µg/L)***
		Median (µg/L)	Range (µg/L)	Median (µg/L)	Range (µg/L)	Median (µg/L)	Range (µg/L)	*Average of two samples*	
Cd	F	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05 – 0.532	≤0.05	0.06
	T	-	-	≤0.05	≤0.05	≤0.05	≤0.05 – 0.621	0.07	
Cu	F	6.65	3.66 – 14.2	3.18	1.96 – 6.19	13.5	6.71 – 109	0.81	1.0
	T	-	-	3.50	2.86 – 6.48	25.3	7.41 – 108	0.92	
Pb	F	0.146	≤0.05 – 0.592	2.66	≤0.05 – 4.89	2.49	1.12 – 27.6	0.1	1.0
	T	-	-	4.06	2.06 – 6.46	11.3	4.35 – 63.3	0.973	
Ni	F	1.53	0.220 – 2.24	0.60	0.1 - 1.6	6.14	1.0 – 20.5	0.27	8
	T	-	-	0.40	0.233 – 0.977	4.99	1.0 – 20.9	0.17	
Zn	F	141	101 – 266	36.6	24.2 – 47.6	235	82.1 – 3750	15.6	2.4
	T	-	-	38.0	30.7 – 77.3	312	88.2 – 3800	6.6	

Notes: * Background stream waters were collected from Streets Creek. Values in red exceed ANZECC Guidelines.

F = Filtered sample

T = Unfiltered sample

Table 4-4: Heavy metal chemistry of road runoff waters, Captain Cook Highway roundabouts (n = 4, February 2003; n = 4, January 2004; n = 4, November 2004). ANZECC Guidelines (2000) for the Protection of Freshwater Ecosystems (99 % Protection Level) are also included. Refer to Chapter 2 – Section 2.5 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

		February 2003		***January 2004***		***November 2004***		***Background stream water* concentrations (µg/L)***	***ANZECC, 2000 (µg/L)***
		Median (µg/L)	Range (µg/L)	Median (µg/L)	Range (µg/L)	Median (µg/L)	Range (µg/L)	*Average of two samples*	
Cd	F	≤0.05	≤0.05	≤0.05	≤0.05 – 0.934	≤0.05	≤0.05	≤0.05	0.06
	T	-	-	≤0.05	≤0.05	≤0.05	≤0.05	0.07	
Cu	F	8.44	4.89 – 12.9	5.50	3.07 – 6.17	13.3	12.3 – 20.6	0.81	1.0
	T	-	-	10.10	3.51 – 14.70	27.8	20.4 – 38.9	0.92	
Pb	F	0.927	0.704 – 1.06	≤0.05	≤0.05 – 0.200	1.49	1.31 – 1.70	0.1	1.0
	T	-	-	5.70	2.76 – 10.2	20.5	10.1 – 39.6	0.973	
Ni	F	0.911	0.209 – 1.99	0.320	0.243 – 1.70	2.84	1.00 – 2.84	0.27	8
	T	-	-	0.800	0.577 – 1.58	3.90	1.00 – 3.48	0.17	
Zn	F	73	50.9 – 117	55.1	40.4 – 65.7	564	282 – 608	15.6	2.4
	T	-	-	76.4	54.6 – 98.3	838	369 – 995	6.6	

Notes: * Background stream waters were collected from Streets Creek. Values in red exceed ANZECC Guidelines.
F = Filtered sample
T = Unfiltered sample

Variable rainfall patterns were noted prior to the sampling events in February 2003, January 2004 and November 2004. Rainfall data for the sampling intervals are shown in Table 4-5.

Table 4-5: Average monthly rainfall data for the Cairns region over the sampling intervals (BOM 2005a).

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4.3.4 Laboratory experiments

4.3.4.1 Column leach experiments

Column leach experiments were conducted on road sediments taken from the Kuranda Range Road and the Captain Cook Highway roundabouts. The details of the column-leach tests were presented in Chapter 2 – Section 2.4.6.1. Cadmium, Cu, Pb, Ni, Zn, Al, Ca and Fe concentrations as well as Eh, dissolved oxygen (DO) and pH were measured in all leachate samples. Furthermore, the time taken for each leachate to pass through the column was recorded. All column-leach data are shown in Figures 4-1 to 4-8.

Metal concentrations showed considerable variation in the column leachates (Figure 4-1, 4-5). For instance, Cd, Cu, Ni, Zn and Ca concentrations in the filtered (<0.45 µm) samples were almost as high as their respective levels in the unfiltered leachates (Figure 4-1, 4-5). In contrast, Pb, Al and Fe values in the filtered samples represented only a small proportion of their total aqueous concentrations (Figure 4-1, 4-5).

Of the elements analysed, Ca was detected in the highest concentrations in the leachates, while Cd was present in the lowest levels (Figure 4-1, 4-5). As with the road runoff waters, Cd concentrations in unfiltered leachates were slightly lower than their respective values in filtered samples. This is ascribed to poor analytical accuracy at low Cd concentrations.

Results from the column leach experiments indicated that heavy metal concentrations generally showed a strong 'first flush' effect in the leachates, particularly those poured through the sediments collected from the Kuranda Range Road (Figure 4-1). Exceptions to the ‘first flush’ effect were exhibited by: a) total Pb and Fe concentrations in the Kuranda Range Road sediment leachates (Figure 4-1); and b) total Cd, Pb, Al and Fe concentrations in the leachates from the Captain Cook Highway roundabout sediments (Figure 4-5).

The cumulative proportion of each heavy metal detected in the column leachates was determined as follows:

$$Mp\ (\%) = ([M]_L \text{ x } 2)/[M]_S \text{ x } 100\ \% \qquad \textbf{(Equation 4-1)}$$

where Mp is the calculated metal proportion, $[M]_L$ is the metal concentration in the leachate (µg/L) and $[M]_S$ is the metal concentration (µg/kg) in the road sediment. The metal values in the leachates were multiplied by a factor of 2 because a liquid/solid ratio of 2:1 was used in the column leach experiments. The cumulative proportions of metals leached from the sediments were calculated for both filtered and unfiltered samples.

Zinc displayed the greatest dissolved values (as represented by the filtered leachates) in the Kuranda Range Road sediments. Approximately 1.2 % of the total Zn content in these sediments was dissolved in the leachates (Figure 4-2). Slightly lower amounts of the total Cu, Cd, Ni and Pb content of these sediments were disssolved in the column leachates (0.7 %, 0.5 %, 0.15 % and 0.1 %, respectively, Figure 4-2).

In contrast, Cd exhibited the greatest dissolved levels in the Captain Cook Highway roundabout sediments; ca. 3.5 % of the total Cd content of these sediments was dissolved (Figure 4-6). By comparison, the dissolved proportions of Zn, Cu, Ni and Pb in these sediments were much lower (1.2 %, 0.5 %, 0.1 % and 0.05 %, respectively, Figure 4-6). Similar patterns were observed for cumulative total metal proportions in the unfiltered leachates (Figure 4-2, 4-6).

The pH values in the leachates progressively increased with increasing volumes of water leached through the columns. This effect was observed in leachates from the both the Kuranda Range Road and Captain Cook Highway roundabout sediments (Figure 4-3, 4-7). In contrast, dissolved oxygen (DO) values marginally decreased with the each volume of water leached through the columns (Figure 4-3, 4-7). Eh values also steadily decreased with the increasing volumes of waters leached through the column containing the Kuranda Range Road sediments (Figure 4-3). By comparison, Eh values initially decreased but then increased in the leachates of the Captain Cook Highway roundabout sediments (Figure 4-7).

The times taken for the leachates to pass through the sediment in the columns were recorded and the results are presented in Figures 4-4 and 4-8. It took approximately 4 minutes for the first 200 mL volume of distilled water to leach through the column containing the Kuranda Range Road sediments (Figure 4-4). The subsequent volumes of water leached through this column required progressively more time to pass through the sediments up to the fifth volume of water. From this point onwards, the remaining volumes of water each consumed the same period of time to pass through the column (approximately 30 minutes each, Figure 4-4).

In comparison, approximately 8 minutes elapsed before the first 200 mL volume of distilled water passed through the column containing the Captain Cook Highway roundabout sediments (Figure 4-8). All subsequent volumes of distilled water required approximately 3 minutes to pass through the sediments in the column (Figure 4-8).

The difference in leaching times between the Kuranda Range Road and the Captain Cook Highway roundabout sediments is attributed to the greater abundance of coarse particles in the Captain Cook Highway roundabout sediments. Settling of the finer sediments from the Kuranda Range Road resulted in the decreased permeability of these sediments over the course of the experiment.

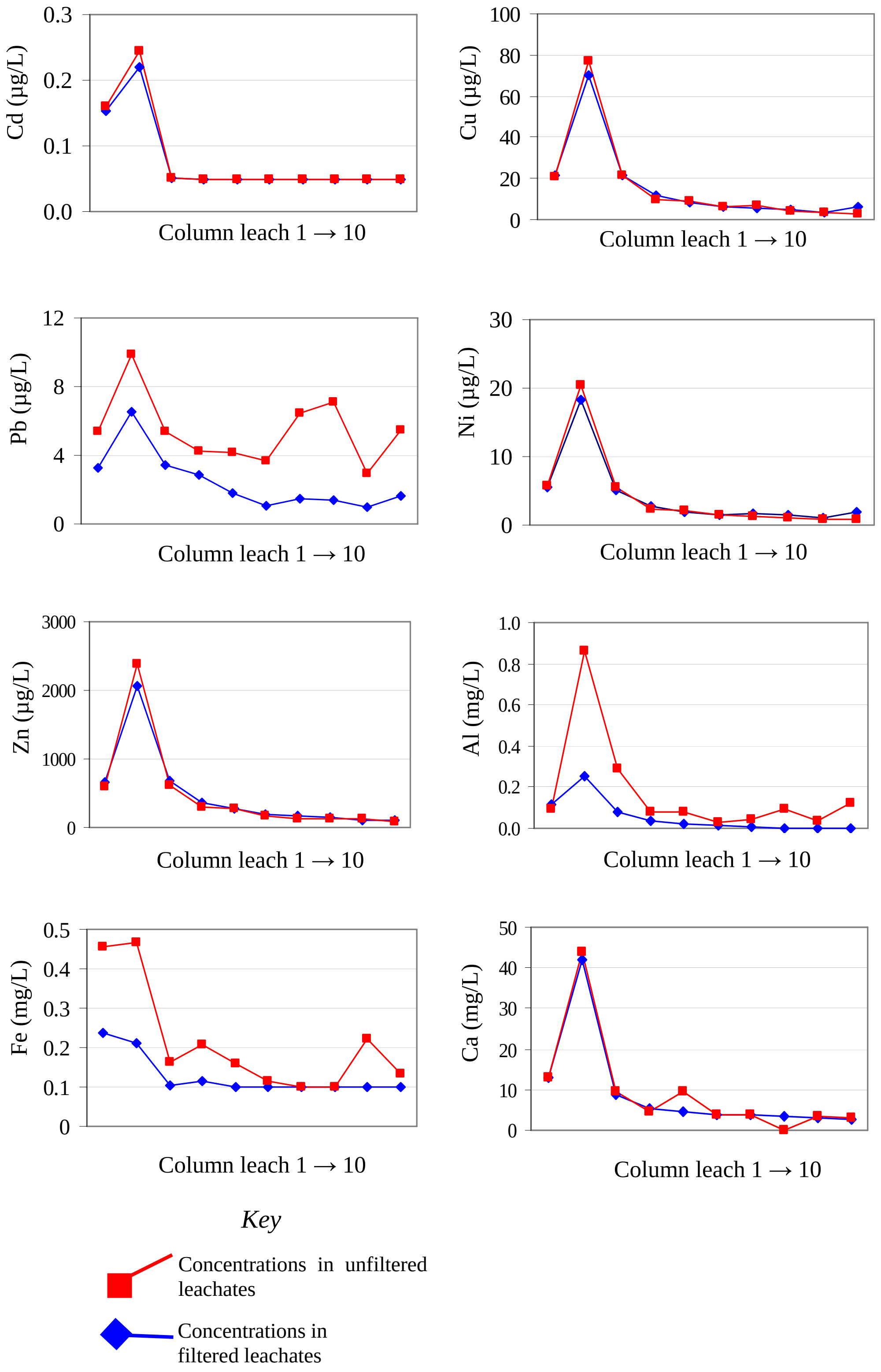

Figure 4-1: Aqueous Cd, Cu, Pb, Ni, Zn, Al, Fe and Ca concentrations in successive column leachates of Kuranda Range Road sediments. Column leachates 1 through to 10 are arranged in order from left to right on the x-axis. Refer to Chapter 2 – Section 2.4.6.1 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

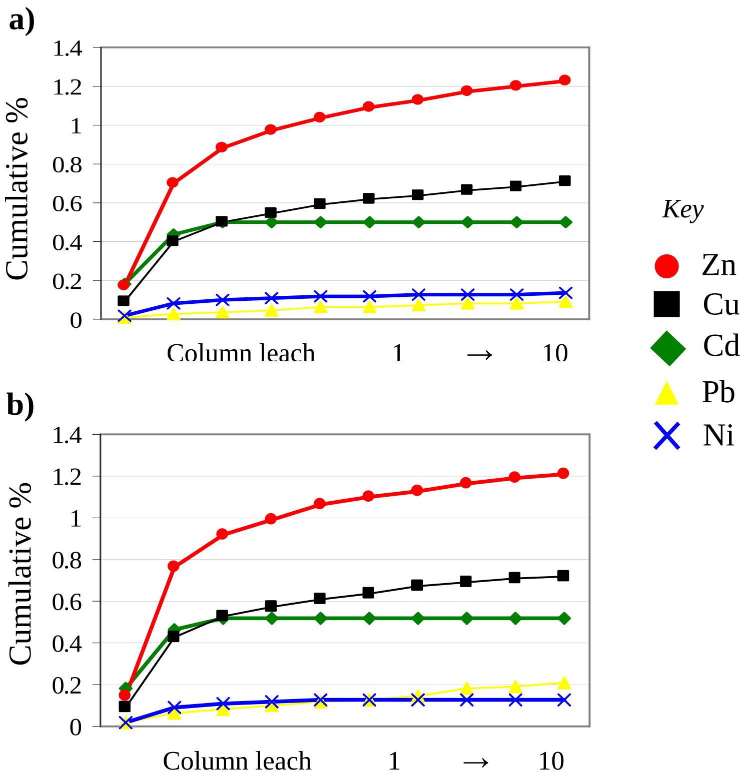

Figure 4-2: Cumulative proportion of metals liberated into column leachates, Kuranda Range Road sediments: a) in filtered leachates; and b) in unfiltered leachates.

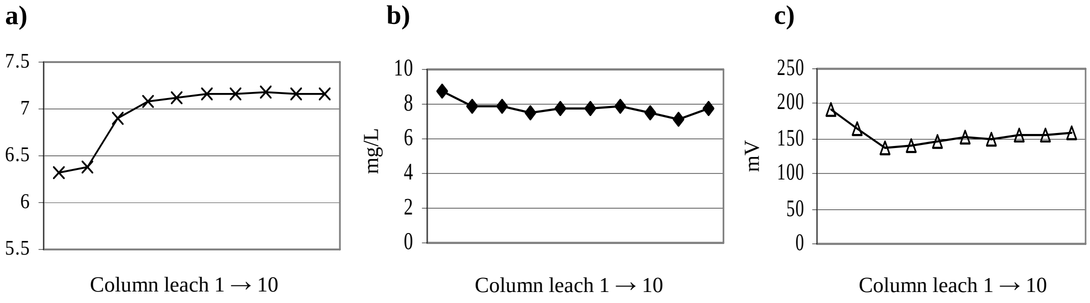

Figure 4-3: a) pH; b) dissolved oxygen (mg/L); and c) Eh (mV) for column leachates, Kuranda Range Road sediments. Refer to Chapter 2 – Section 2.4.6.1 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

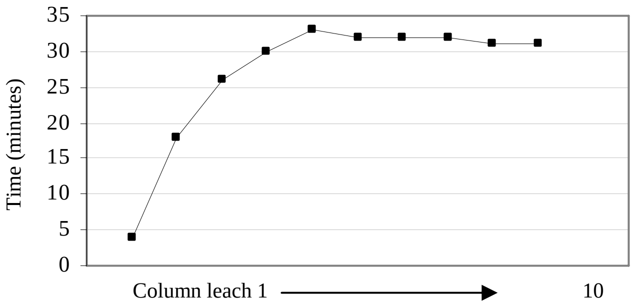

Figure 4-4: Time taken (minutes) for leachate volumes to pass through sediments in the column containing Kuranda Range Road sediments.

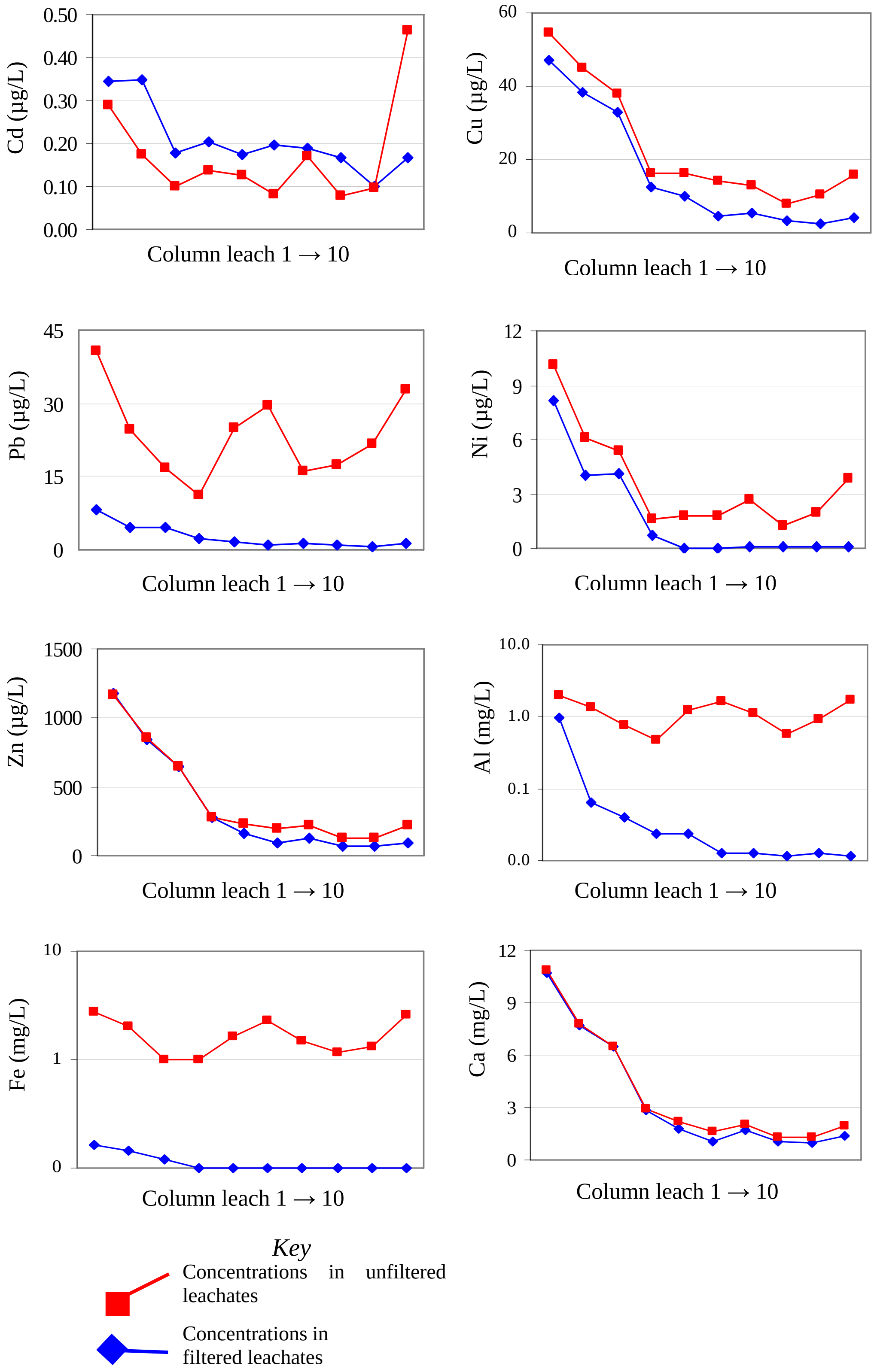

Figure 4-5: Aqueous Cd, Cu, Pb, Ni, Zn, Al, Fe and Ca concentrations in successive column leachates of Captain Cook Highway roundabout sediments. Column leachates 1 through to 10 are arranged in order from left to right on the x-axis. Refer to Chapter 2 – Section 2.4.6.1 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

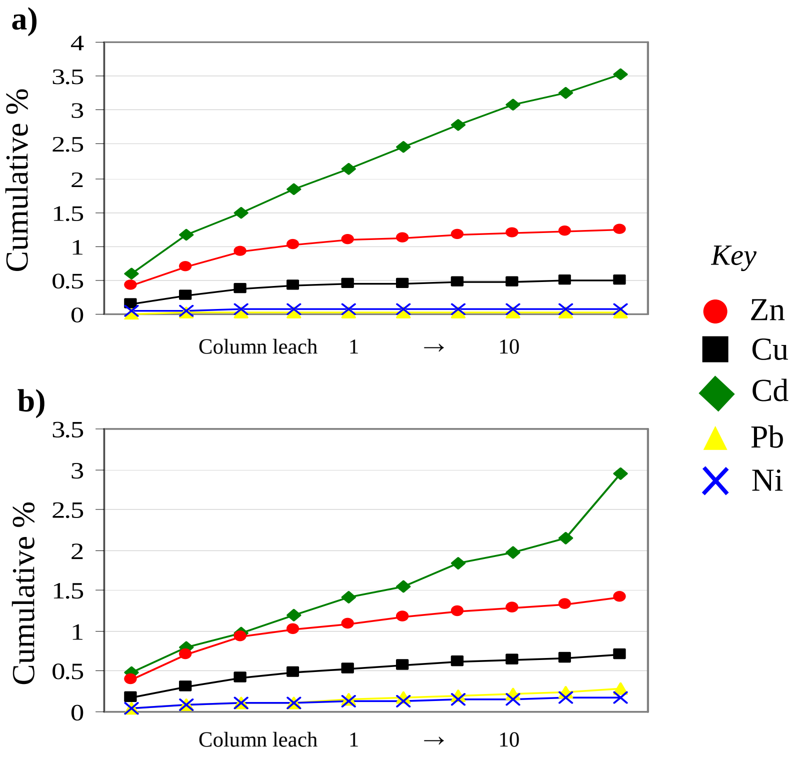

Figure 4-6: Cumulative proportion of metals liberated into column leachates, Captain Cook Highway roundabout sediments: a) in filtered leachates; and b) in unfiltered leachates.

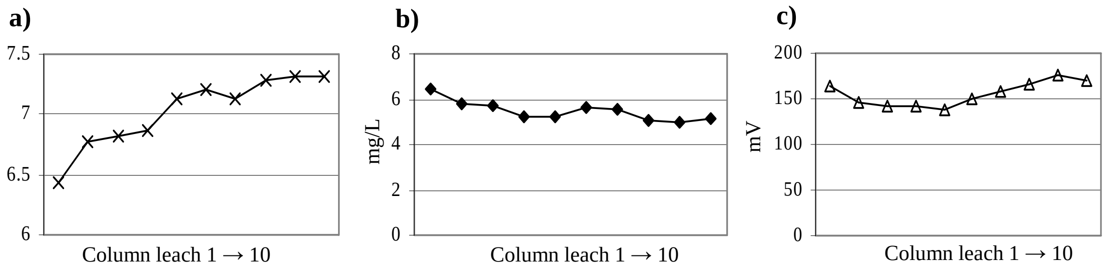

Figure 4-7: a) pH; b) dissolved oxygen (mg/L); and c) Eh (mV) for column leachates, Captain Cook Highway roundabout sediments. Refer to Chapter 2 – Section 2.4.6.1 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

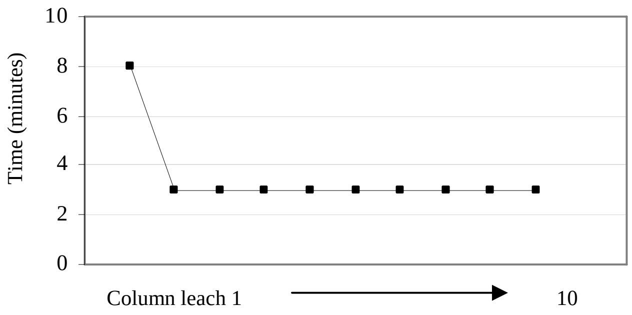

Figure 4-8: Time taken (minutes) for leachate volumes to pass through sediments in the column containing Captain Cook Highway roundabout sediments.

4.3.4.2 Ponding experiments

The set-up of the ponding experiments was described in Chapter 2 – Section 2.4.6.2. The concentration data for Cd, Cu, Pb, Ni, Zn, Al, Ca and Fe in the pond decant waters from the Kuranda Range Road sediments and the Captain Cook Highway roundabout sediments are shown in Figures 4-9 and 4-12, respectively.

Individual aqueous metal concentrations varied in the pond decant waters (Figure 4-9, 4-12). Similar to the column leach experiments, Ca was detected in the highest levels in the pond waters and Cd was present in the lowest concentrations (Figure 4-9, 4-12).

The metal concentrations detected in the filtered pond samples were generally much lower than those concentrations in the unfiltered waters. Additionally, the release of individual metals from the road sediments into the pond decant waters fluctuated over time. The following trends were observed for element concentrations in the pond decant waters from the Kuranda Range Road sediments (Figure 4-9):

- The Cd and Cu concentrations in filtered and unfiltered waters initially increased (24 hours), then decreased (1 week) before rising again in the final sample (1 month).
- The Ni, Zn concentrations in the filtered and unfiltered waters initially rose (1 week) but then decreased over the sampling period (1 month).
- The Pb and Al concentrations in the unfiltered samples decreased continuously in the pond decant samples over the course of the experiment (1 month).
- The Pb and Al content in the filtered samples initially increased (1 week) but finally decreased over the sampling period (1 month).
- Calcium levels steadily increased in the filtered and unfiltered waters from the beginning (5 minutes) to the end of the experiment (1 month).

- Iron concentrations in the unfiltered samples initially decreased (24 hours) but gradually increased (1 month), while Fe levels in the filtered waters steadily increased over the duration of the experiment (1 month).

Cadmium, Cu and Fe concentrations were observed to increase in the final sample (1 month) obtained during the Kuranda Range Road sediment ponding experiment. Hence, the ponding experiment conducted on the road sediments collected from the Captain Cook Highway roundabouts was carried out over a 3 month period. This was done to investigate long-term trends in Cd, Cu and Fe concentrations in the pond waters. Patterns noted for element values in the pond decant waters from the Captain Cook Highway roundabout sediments (Figure 4-12) are summarised forthwith:

- Cadmium, Cu, Ni and Zn concentrations gradually decreased in unfiltered waters to the end of the experiment (3 months).
- In contrast, the levels of Cd, Cu, Ni and Zn in the filtered samples initially increased (up to a period of 1 week) before finally decreasing at the cessation of the sampling period (3 months).
- Lead, Fe and Ca concentrations fluctuated in filtered and unfiltered samples over the course of the experiment.
- Aluminium levels steadily decreased in the filtered and unfiltered pond decant waters over the 3 months.

The cumulative proportion of each heavy metal analysed in the pond decant waters was calculated using Equation 4-1 (Section 4.3.4.1). Dissolved proportions of metals (i.e. those determined from metal values in the filtered samples) in the pond waters from the Kuranda Range Road sediments were 0.9 %, 0.6 %, 0.3 %, 0.2 % and 0.05 % of the total Zn, Cd, Ni, Cu and Pb sediment contents (Figure 4-10). These proportions were remarkably similar to dissolved values calculated from the column leachates of the Kuranda Range Road sediments (Figure 4-2).

For the Captain Cook Highway roundabout sediments, dissolved metal proportions in the pond decant waters were higher than those values calculated for the column leachates. For example, ca. 3.5 % of the total Cd content of the Captain Cook Highway roundabout sediments was dissolved in the column leachates (Figure 4-6) as opposed to 6 % of total Cd being dissolved in the pond decant waters (Figure 4-13). Lesser amounts of the other metals were dissolved in the pond decant waters of the Captain Cook Highway roundabout sediments (Zn 2 %, Cu 0.8 %, Ni 0.5 % and Pb 0.05 % dissolved) (Figure 4-13).

Metal proportions in the unfiltered pond waters were generally similar to metal levels in the filtered waters (Figure 4-10, 4-13). However, total Zn levels in the pond waters from the Captain Cook Highway roundabout sediments were much higher than the Zn values recorded in the filtered waters (Figure 4-13).

pH values steadily increased over time in the samples ponded with the Kuranda Range Road sediments and the Captain Cook Highway roundabout sediments (Figure 4-11, 4-14). In contrast, DO and Eh values showed consistent temporal decreases in the pond decant waters (Figure 4-11, 4-14).

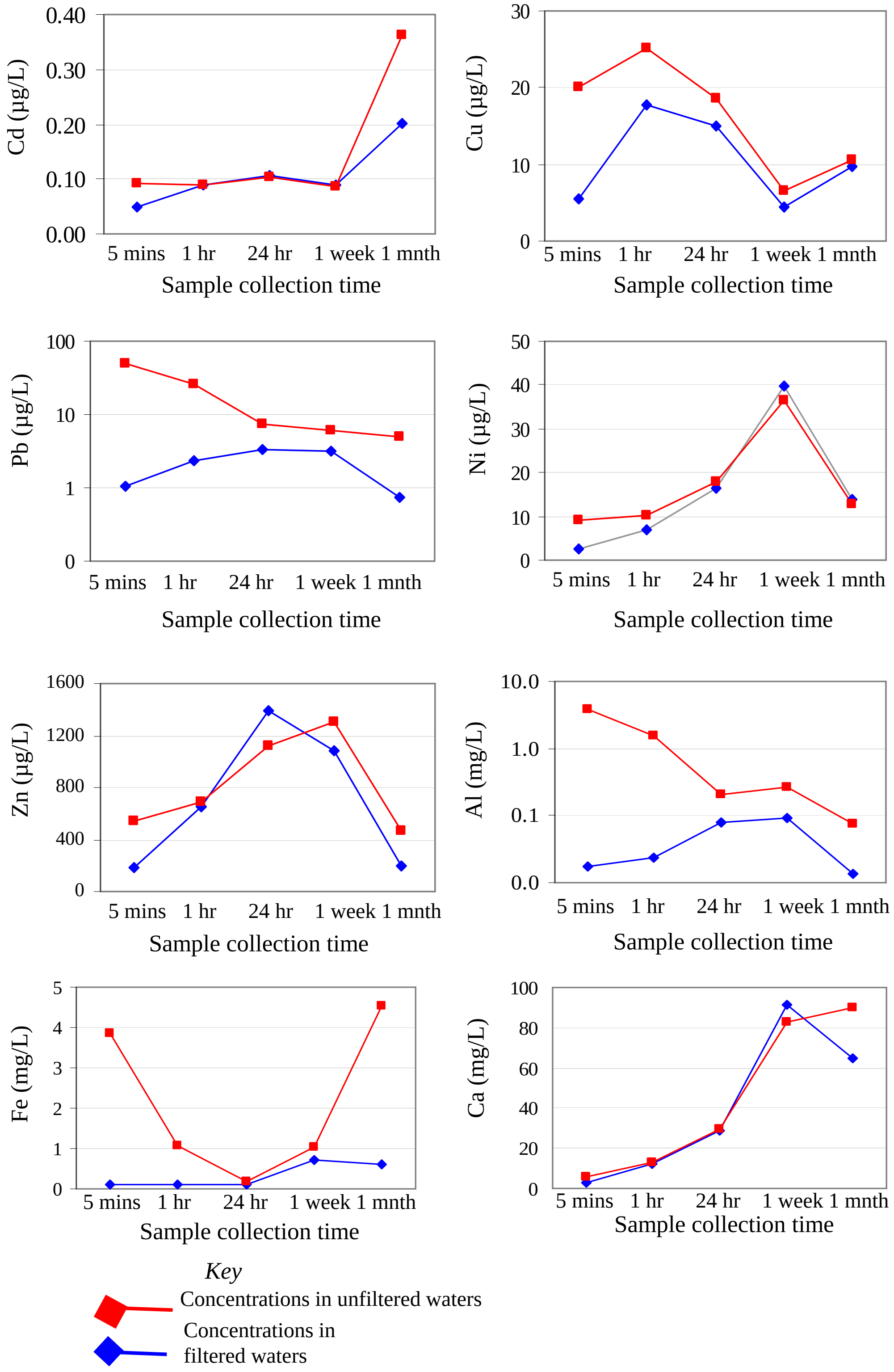

Figure 4-9: Aqueous Cd, Cu, Pb, Ni, Zn, Al, Fe and Ca concentrations in successive pond decant water samples, Kuranda Range Road sediments. Sample intervals are plotted on the x-axis. Refer to Chapter 2 – Section 2.4.6.2 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

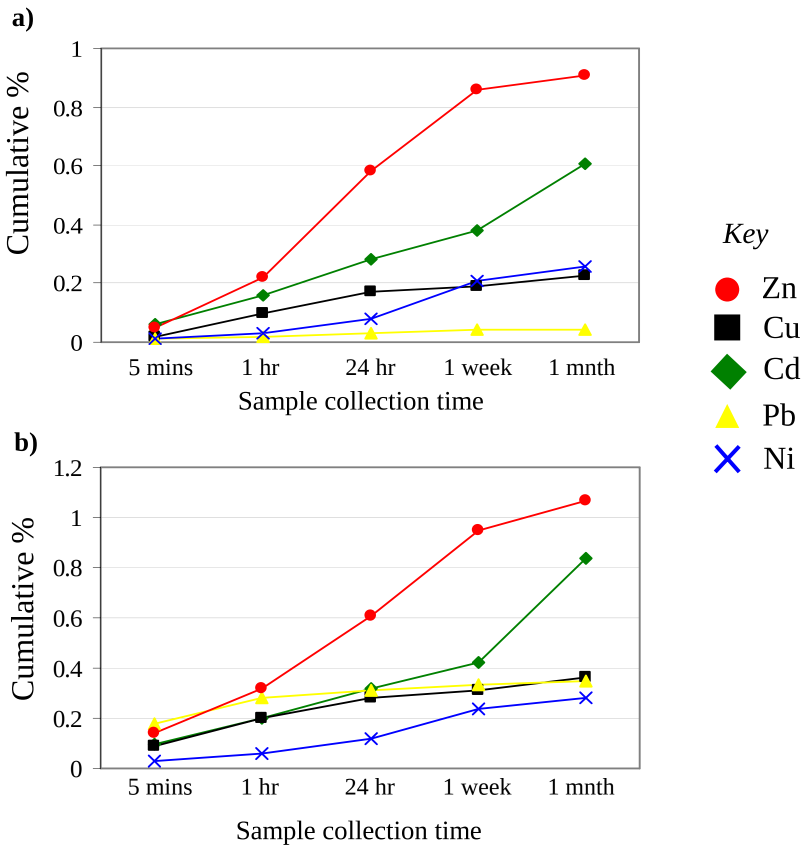

Figure 4-10: Cumulative proportions of metals liberated into pond decant waters, Kuranda Range Road sediments: a) in filtered waters; and b) in unfiltered waters.

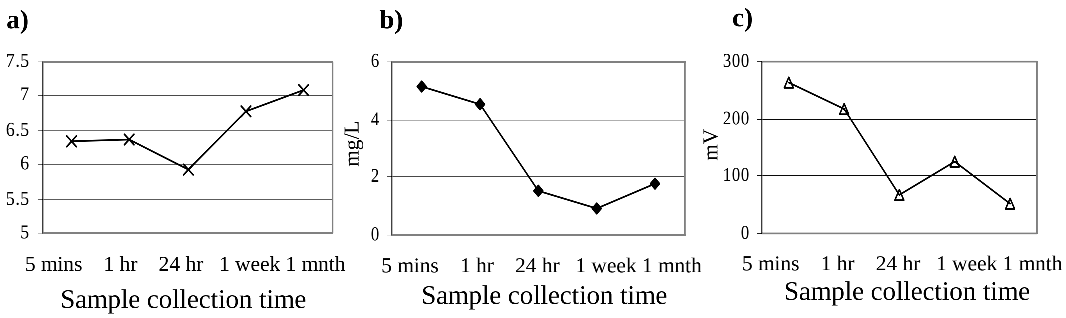

Figure 4-11: a) pH; b) dissolved oxygen (mg/L); and c) Eh (mV) for pond decant waters, Kuranda Range Road sediments. Refer to Chapter 2 – Section 2.4.6.2 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

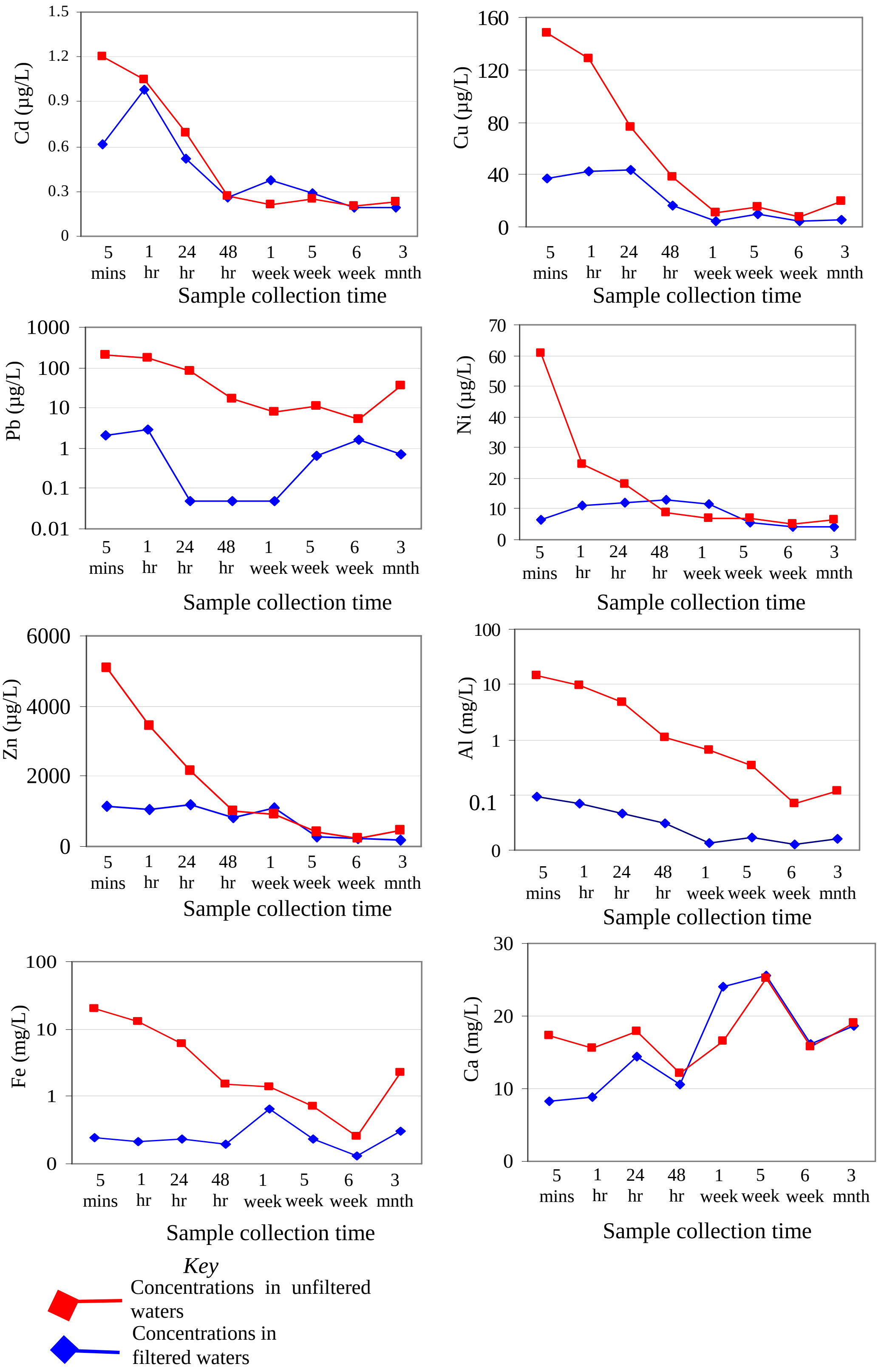

Figure 4-12: Aqueous Cd, Cu, Pb, Ni, Zn, Al, Fe and Ca concentrations in successive pond decant water samples, Captain Cook Highway roundabout sediments. Sample intervals are plotted on the x-axis. Refer to Chapter 2 – Section 2.4.6.2 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

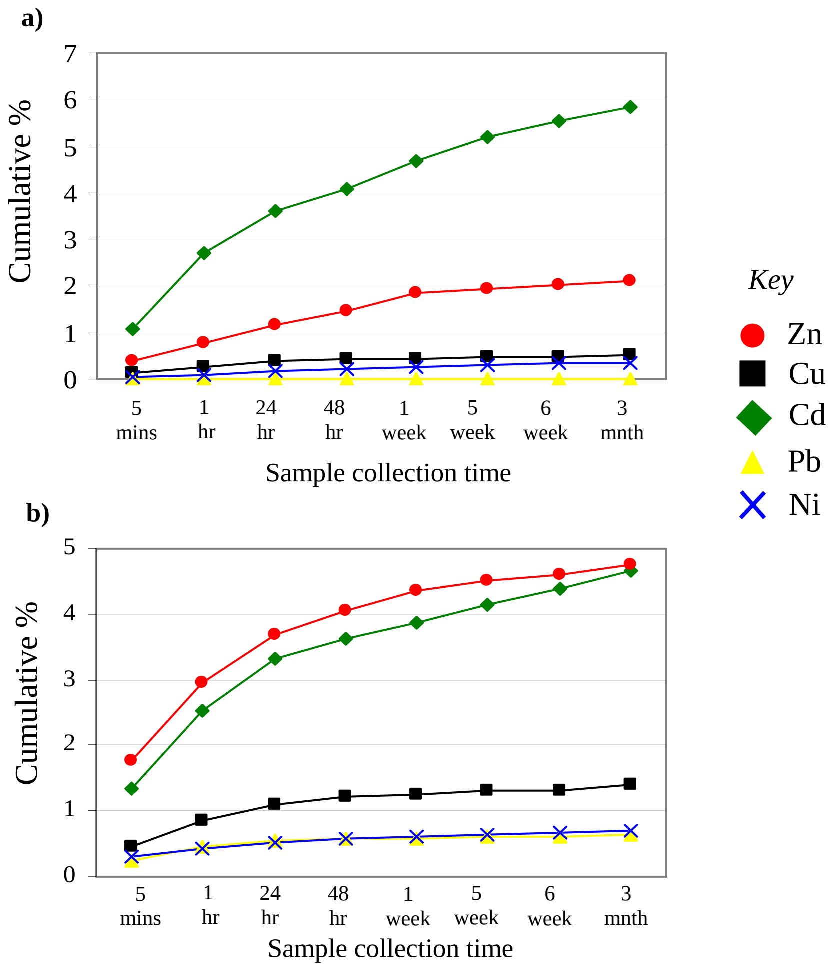

Figure 4-13: Cumulative proportions of metals liberated into pond decant waters, Captain Cook Highway roundabout sediments: a) in filtered waters; and b) in unfiltered waters.

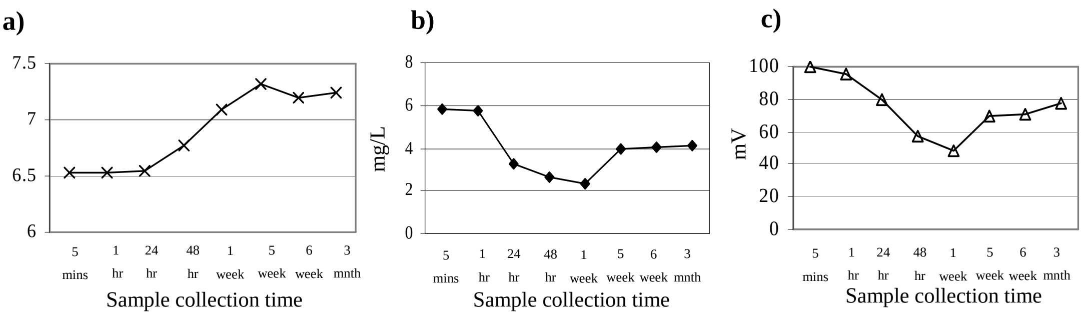

Figure 4-14: a) pH; b) dissolved oxygen (mg/L); and c) Eh (mV) for pond decant waters, Captain Cook Highway roundabout sediments. Refer to Chapter 2 – Section 2.4.6.2 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

4.3.4.3 Tyre ponding experiment

The waters ponded with the car and truck tyre shreds (see Chapter 2, Section 2.6 for methodology) were analysed for their Cd, Cu, Pb, Ni and Zn concentrations. Individual metal values varied in the waters ponded with the tyre shreds (Figure 4-15). Zinc was present in the highest concentrations (above 500 µg/L) in all samples (Figure 4-15). In contrast, Cd was below detection in each decant sample (Figure 4-15). It was also noted that the concentrations of metals released from the car tyre shreds were higher than those levels derived from the truck tyre shreds (Figure 4-15).

The results indicate that considerable amounts of Zn were continuously liberated from tyre rubber shreds in distilled water over a period of 1 month. Zinc values progressively increased in both the car and truck tyre pond waters over the duration of the experiment (Figure 4-15). Concentrations of the other heavy metals steadily decreased in the pond waters over time, with the exception of Ni (Figure 4-15). Nickel concentrations rapidly dropped after 5 minutes but then gradually increased up to a period of 1 month in both the car and truck decant waters (Figure 4-15). The pH values in the tyre rubber (car and truck) decant samples increased over the sampling period (Figure 4-16). Conversely, Eh values consistently decreased in the pond samples (Figure 4-17).

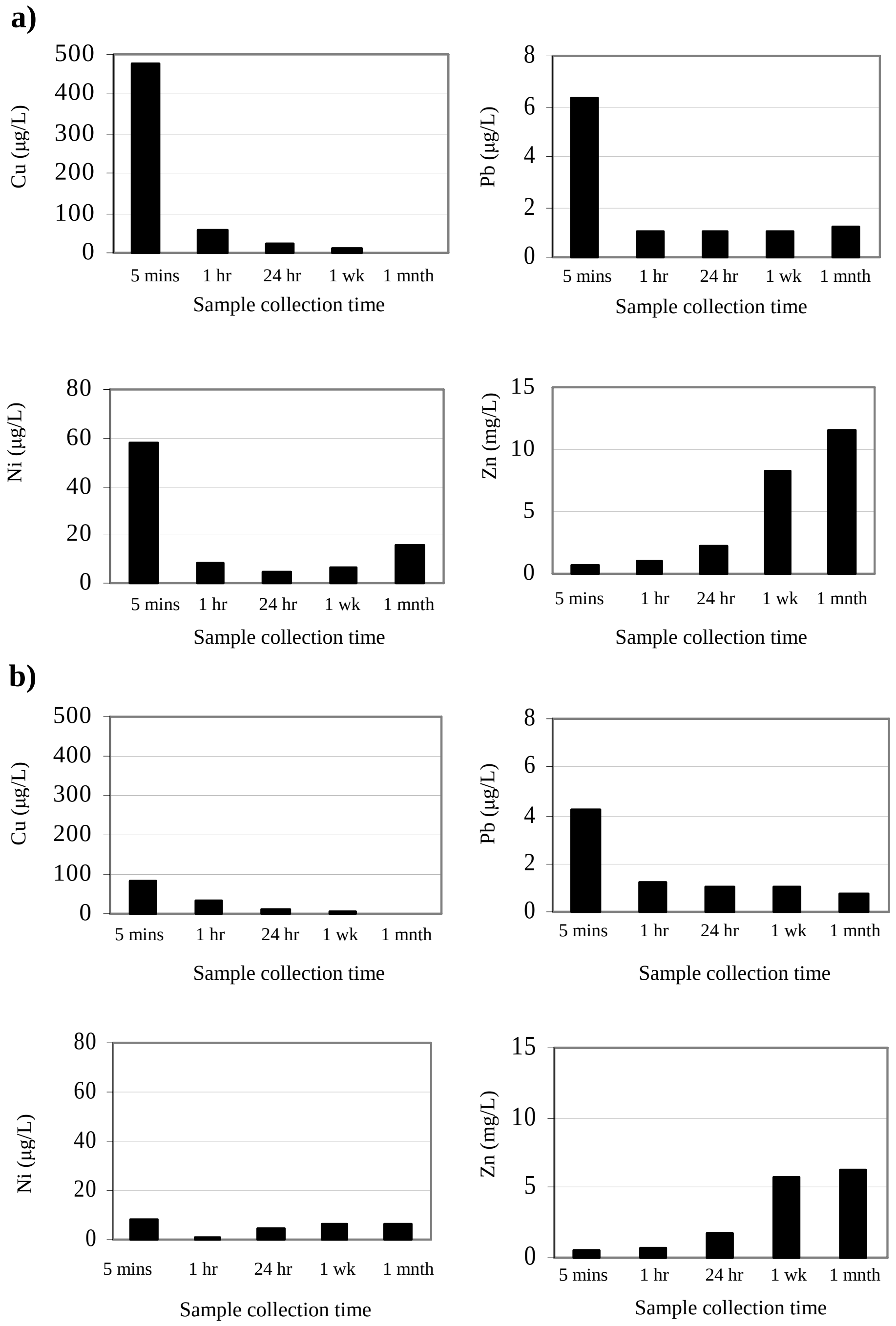

Figure 4-15: Aqueous metal concentrations in filtered pond decant waters: a) ponded with car tyre shreds; and b) ponded with truck tyre shreds. Refer to Chapter 2 – Section 2.6 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

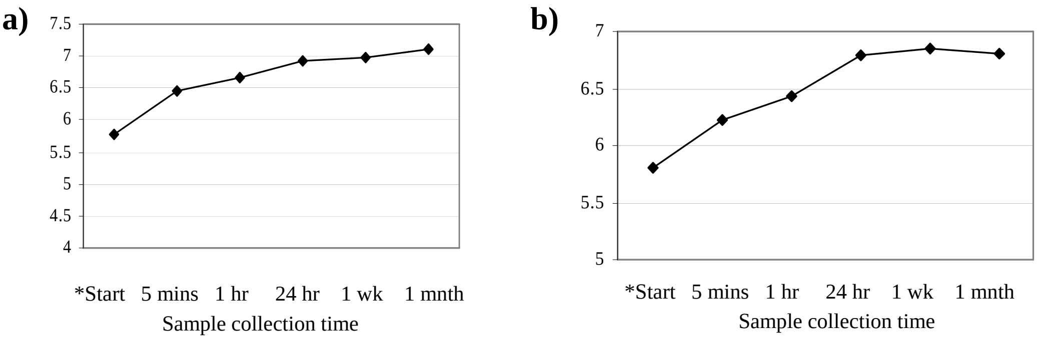

Figure 4-16: pH in: a) water ponded with car tyre shreds; and b) water ponded with truck tyre shreds. **Start refers to sample of distilled water analysed prior to the commencement of the experiment.* Refer to Chapter 2 – Section 2.6 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

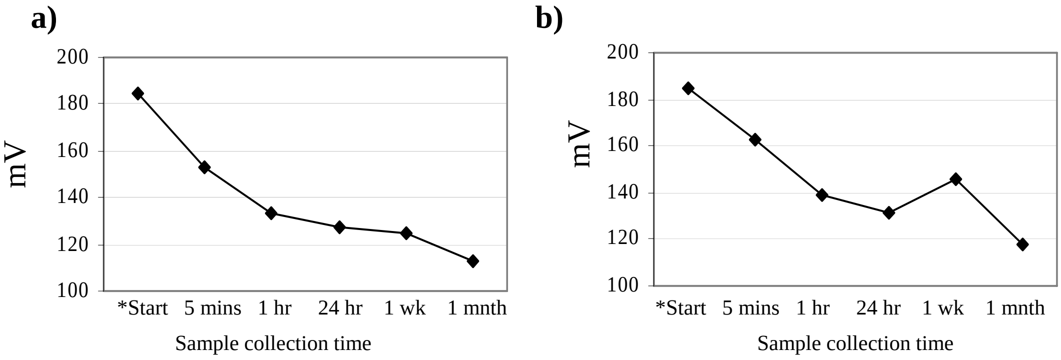

Figure 4-17: Eh (mV) in: a) water ponded with car tyre shreds; and b) water ponded with truck tyre shreds. **Start refers to sample of distilled water analysed prior to the commencement of the experiment.* Refer to Chapter 2 – Section 2.6 for sample preparation details. Appendix A presents sample ID and the data are given in Appendix B.

4.4 Discussion

4.4.1 Road runoff waters

4.4.1.1 General concentration trends

Elevated aqueous metal concentrations, above ANZECC Guidelines (2000) for the Protection of Freshwaters (99 % Protection Level), were detected in filtered and unfiltered road runoff water samples taken from the project area. However, it is important not to place too great an emphasis on environmental guidelines for a number of reasons. For instance, the ANZECC investigation levels indicated in Table 4-3 and 4-4 apply to freshwater stream systems, not to road runoff waters. It is reasonable to anticipate that the contaminant concentrations in road runoff waters will be diluted upon mixing with freshwater systems. Secondly, environmental guidelines do not take into account the bioavailability or reactivity of contaminants. In the case of this study, it is not known if the entire fraction of heavy metals detected in the filtered road runoff water samples will be available for uptake by organisms that ingest these waters. As previously discussed, the dissolved component of metals, as determined by filtering through 0.45 µm filter paper, may actually include small inert colloidal particles that are not readily incorporated into organic tissue (Siegel 2002). Finally, the ANZECC threshold values do not take into account variations in water chemistry between different catchments. In this study, aqueous Zn values in the headwaters of Streets Creek (upgradient of roads) were in excess of the ANZECC (2000) threshold values for Freshwater Ecosystems (99 % Protection Level). However, these Zn values in the studied creek were viewed to represent naturally-occurring levels, as they were detected in waters collected upstream of any anthropogenic metal sources. Consequently, environmental investigation guidelines are best used as triggers for more detailed investigations.

Nonetheless, the results of this study confirm that metal contaminants are mobilised by road runoff waters which pass over road surfaces during rainfall events. These metals, which are originally derived from diverse sources (e.g.

bitumen, vehicle exhaust and tyres), are deposited on the road surface as fine dust particles as well as coarser sediments. The partial dissolution and suspension of these dusts and sediments results in the liberation of traffic-derived metals in road runoff waters.

The data presented in Table 4-6 compare the results of this study with road runoff water metal values recorded in other investigations. Cadmium concentrations in the road runoff waters analysed in this research were in the realm of the lower detection limit of the ICP-MS analytical technique. Consequently, it is difficult to make meaningful comments on the distribution of this metal in the road runoff waters examined by this study. By comparison, Cu, Pb, Ni and Zn values in filtered and unfiltered road runoff waters in this project were much higher than aqueous Cd levels. In fact, Cu, b, Ni and Zn concentrations were similar to those documented in road runoff waters from more populated regions (Table 4-6). Moreover, the maximum Zn concentrations detected in filtered and unfiltered samples taken from the Kuranda Range Road in November 2004 were higher than those Zn levels reported in road runoff waters examined from busy roads and highways in the UK, the USA and Italy (Table 4-6).

Table 4-6: Metal concentrations in road runoff waters, values compiled from the literature.

		Mean concentration ($\mu g/L$)	*Concentration range ($\mu g/L$)*	*Location*	*Author*
Cd	T	37	0.4 – 220	Birmingham, UK	Pitt et al. (1995)
	F	0.3	0.1 – 0.6		
	T	0.7		Gold Coast, Australia	Drapper et al. (1997)
			2 – 49	Sydney, Australia	
	T		0.026 – 0.27	Sweden	Backstrom et al. (2003)
	F		0.02 – 0.26		
	T	(median value) ≤0.05	≤0.05 – 0.621	Kuranda Range Road, Nov 04	This study
	F	(median value) ≤0.05	≤0.05 – 0.532		
Cu	T	280	10 – 1250	Birmingham, UK	Pitt et al. (1995)
	F	3.8	1 – 11		
	T		187 – 588	Central Italy	Mangani et al. (2005)
	F		6 – 86		
	T	429		UK	Muhammad et al. (2004)
	T		40 – 260	Port of Brisbane, Australia	Toomey et al. (2003)
	T	27		Gold Coast, Australia	Drapper et al. (1997)
			8 – 327	Sydney, Australia	
		230		Brisbane, Australia	
	T		7 – 66	Sweden	Backstrom et al. (2003)
	F		6 – 60		
	F	(median value) 16.9		Atlanta, USA	Rose et al. (2001)
	T	(median value) 25.3	7.41 – 108	Kuranda Range Road, Nov 04	This study
	F	(median value) 13.5	6.71 – 109		
Pb	T	720		UK	Muhammad et al. (2004)
	T	61		Gold Coast, Australia	Drapper et al. (1997)
			22 – 439	Sydney, Australia	
		500		Brisbane, Australia	
	T		151.73 – 277.46	Central Italy	Mangani et al. (2005)
	F		0.00 – 3.77		
	T	43	1.5 – 150	Birmingham, UK	Pitt et al. (1995)
	F	2.0	1.1 – 3.9		
	T		100 – 430	Port of Brisbane, Australia	Toomey et al. (2003)
	T		5.25 – 18	Sweden	Backstrom et al. (2003)
	F		0.45 – 3.0		
	F	(median value) 11.4		Atlanta, USA	Rose et al. (2001)
	T	(median value) 11.30	4.35 – 63.3	Kuranda Range Road, Nov 04	This study
	F	(median value) 2.49	1.12 – 27.6		
Ni	T	17	1.2 – 70	Birmingham, UK	Pitt et al. (1995)
	T	2		Gold Coast, Australia	Drapper et al. (1997)
	F	(median value) 4.0		Atlanta, USA	Rose et al. (2001)
	T	(median value) 4.99	1.0 – 20.9	Kuranda Range Road, Nov 04	This study
	F	(median value) 6.14	1.0 – 20.5		
Zn	T	1699		UK	Muhammad et al. (2004)
	F	(median value) 905	88 – 4019	Atlanta, USA	Rose et al. (2001)
	T		1087.36 – 2930	Central Italy	Mangani et al. (2005)
	F		0.00 – 132.95		
	T	58	4.0 – 130	Birmingham, UK	Pitt et al. (1995)
	F	31	4.0 – 76.0		
	T		185 – 1400	Port of Brisbane, Australia	Toomey et al. (2003)
	T	17		Gold Coast, Australia	Drapper et al. (1997)
			35 – 1576	Sydney, Australia	
		1700		Brisbane, Australia	
	T		41 – 180	Sweden	Backstrom et al. (2003)
	F		43.5 – 100		
	T	(median value) 312	88.2 – 3800	Kuranda Range Road, Nov 04	This study
	F	(median value) 235	82.1 – 3750		

Notes: T = total concentration, F = concentration in filtered sample

4.4.1.2 'Dissolved' metal values in road runoff waters

It is important to reiterate here that 'dissolved' metals refer to those metals which are able to pass through a 0.45 μm membrane filter. As such, it is highly likely that the resulting filtrate contains complexed and colloidal metals as well as dissolved ionic species. However, the term 'dissolved' is still used to refer to those metals in the 0.45 μm filtrate because filtering is considered to be the technique that is best able to isolate the mobile fraction of metals in water samples (Rose et al. 2001). By comparison, 'particulate' metals are reported as those which are unable to pass through a 0.45 μm membrane filter.

Copper

In this study, Cu levels in the filtered samples were similar to Cu levels in unfiltered road runoff waters. Consequently, a large portion of this Cu is interpreted to be dissolved. Thus, Cu is likely mobile in road runoff waters along the Kuranda Range Road and the Captain Cook Highway roundabouts. The road runoff waters potentially transport dissolved Cu into adjoining catchments.

Few other studies have shown Cu to be strongly dissolved in road runoff waters (e.g. Dierkes and Geiger 1999, Backstrom et al. 2005). However, a number of investigations have pointed to Cu being predominantly associated with coarser, particulate phases in road runoff waters (e.g. Pitt et al. 1995, Mangani et al. 2005).

Lead

In the road runoff water samples collected in this investigation, Pb concentrations in filtered samples were generally much lower than the Pb levels in unfiltered samples. This conforms to the commonly observed trend that Pb in road runoff waters is generally associated with suspended particulates and complexes which are greater than 0.45 μm in diameter (Table 4-6). Lead has been widely documented to be insoluble in near-neutral pH road runoff waters (Bourcier 1979; Sansalone and Buchberger 1997).

Nickel

Nickel levels in filtered waters were commonly much lower that total Ni levels in road runoff waters collected from the Kuranda Range Road (Table 4-6). Hence, most of the Ni in these waters is likely associated with particulates. However, it is difficult to compare the results of this study with other investigations as very little research has been conducted on the aqueous mobility of Ni in road runoff waters.

Zinc

This research revealed that Zn concentrations in the unfiltered road runoff water samples were only marginally higher than the Zn levels in corresponding filtered waters. The Zn concentrations in the filtered road runoff waters from the Kuranda Range Road represented approximately 70 – 95 % of the total Zn content in the samples, whereas 70 – 75 % of the total Zn content of the road runoff water samples collected from the Captain Cook Highway roundabouts was present in the 0.45 μm filtrate. These results suggest that Zn is largely dissolved in the studied road runoff waters. Data from the literature indicate that dissolved values of Zn in road runoff waters are highly variable between locations with different climates (Table 4-6). For example, in a dry Mediterranean climate in Italy, Zn in road runoff waters was shown to be relatively insoluble in road runoff waters (Mangani et al. 2005). In contrast Zn in road runoff waters was largely dissolved in Britain, a much wetter location than central Italy (Pitt et al. 1995).

4.4.1.3 Dilution effect on metal concentrations in road runoff waters

There are a number of factors that control spatial and temporal variations in heavy metal concentrations in road runoff waters. These include: traffic volume (Backstrom et al. 2003); local microclimatic conditions (Thakur et al. 2004); road drainage design (Sansalone and Buchberger 1997); intensity of flushing events (Bourcier 1979); and time (ADD period) between flushing events (Birch and Scollen 2003). These last two parameters are particularly pertinent to wet-dry tropical regions, which experience intense episodes of rainfall over short intervals. In this study, metal concentrations in road runoff waters were analysed during a number of rainfall events (February 2003, January 2004 and November 2004), in order to elucidate the impacts of rainfall intensity and the ADD period on metal concentrations in road runoff waters.

In the Cairns region, the average monthly rainfall for the three months prior to February 2003 and January 2004 was much greater than the average monthly rainfall for the three months prior to November 2004 (Table 4-5). Moreover, an ADD period of 27 days had passed prior to the collection of the November 2004 samples. In contrast, there was an ADD period of just 5 days leading up to the acquisition of the in February 2003 and January 2004 road runoff waters. Metal concentrations in the road runoff samples collected in February 2003 and January 2004 were much lower than those values in the samples taken in November 2004. Hence, the most plausible factors that may account for these disparities in aqueous metal concentrations are: a) variations in the intensity of the rainfall events during the sampling rounds; and b) differences in the length of the ADD periods leading up to the various rainfall events in which the road runoff water samples were acquired.

The low rainfall volume preceding November 2004 likely permitted the accumulation of metal-bearing sediments on the road surface. The importance of a dry period in accommodating sediment build-up on roads has been documented in previous research (e.g. Birch and Scollen 2003, Thakur et al. 2004).

Conversely, the higher volume of rainfall experienced in the Cairns region prior to February 2003 and January 2004, likely resulted in the leaching of a considerable portion of metals from the road surface. The dilution of metal contaminant concentrations in road runoff waters following the onset of heavy rain has been documented by Sansalone and Buchberger (1997). Their research demonstrated that contaminant concentrations in road runoff waters reach a maximum (i.e. ‘first flush’ levels) shortly following the onset of a rainfall event (Figure 4-18). Subsequently, contaminant concentrations rapidly decrease due to dilution.

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Figure 4-18: The 'first flush' model for contaminant concentrations in road runoff waters (modified from Sansalone and Buchberger 1997).

Despite the recognised occurrence of the 'first flush' trend, Soller et al. (2005) found no 'first flush' effect for dissolved (i.e. filtered through a 0.45 µm membrane) metal concentrations in road runoff waters captured during several storm events in the USA. Their research highlighted problems in the definition of 'first flush' rainfall events, which they interpreted to be "the first substantial storms of the … wet seasons" (Soller et al. 2005). Although several of their 'first flush' storms signified the first intense rainfall events of the season, they were in fact preceded by very short ADD periods. Furthermore, a number of the rainfall events documented by the authors as "baseline storms" followed prolonged ADD periods. Hence, dissolved metal concentrations in the runoff waters collected during the 'first flush' storms were not notably elevated above metal values in waters samples during the "baseline storms" (Soller et al. 2005). Thus, it is clear that the ADD period is a critical factor in defining a 'first flush' rainfall event.

In fact, even following a very brief ADD interval, elevated metal values may be present in road runoff waters. For example, the results of this study revealed high Cu and Zn concentrations (above ANZECC Guidelines, Freshwater Ecosystems, 99 % Protection Level, 2000) in the road runoff waters collected in February 2003 and January 2004. This was despite the very short ADD periods (few days) recorded prior to these sampling events. These findings clearly demonstrate that runoff waters cannot remove the total reservoir of metals from road surfaces. This is because the accumulation of contaminants in road sediments is a constant process (Birch and Scollen 2003). Vehicles continue to use roads in the rain and contaminant output is sustained during rainfall events. In fact, the capture of atmospheric metal-bearing dust particles by rain drops has been documented by Rohbock (1981). These rain drops transport metals to the road surface where they are incorporated into road runoff waters.

The rate of contaminant output and subsequent accumulation on road surfaces is strongly dependent on rainfall intensity, with greater rates of build-up occurring during an ease in rainfall (Rohbock 1981). The fact that metals continue to settle on roads during rainfall is further supported by results of Bourcier (1979), who examined heavy metal removal by runoff waters from road surfaces in Washington State, USA. Findings of that particular study revealed that metals may accumulate faster on road surfaces than they are removed by road runoff waters during a storm event (Bourcier 1979).

In summary, this study has shown that 'first flush' road runoff waters mobilise high levels of dissolved and suspended metals. Moreover, continued heavy rainfall is an important factor in reducing metal concentrations in road runoff waters within wet-dry tropical locations. However, results of this research have also clearly demonstrated that metal contaminants persist in road runoff waters even after the onset of intense rainfall. This has an important implication for wet-dry tropical locations because it indicates that road runoff waters that occur late in the 'wet season' continue to mobilise metals, albeit in lower concentrations, from road surfaces to surrounding environments. The road runoff water results highlight a paradox with the results of the sequential extraction discussed in Chapter 3, where most metals associated with road sediments were found to be in highly immobile fractions. This suggests that rainwater runoff is capable of dissolving metal fractions associated with tyre rubber shreds on road surfaces. Causes of this dissolution are unknown and should be further explored.

4.4.1.4 Significance of pH in road runoff waters

Road runoff water pH is an extremely important parameter influencing the solubility of metals (Sansalone and Buchberger 1997). For example, Rose et al.

(2001) investigated the mobility of metals in urban stormwater runoff in Atlanta, USA. They found that the near-neutral pH of the road runoff waters was critical in inducing the adsorption of soluble Zn onto suspended oxyhydroxide surfaces (Rose et al. 2001). The solubility of Zn, thus, was found to be greatly reduced as this sorption process presumably led to the removal of Zn from the stream waters. Furthermore, research by Munk and Faure (2004) showed variations in the concentrations of metals in stream waters may be affected by pH changes of as little as 0.2 units (Munk and Faure 2004).

In this study, relationships between metal concentrations and pH values in the road runoff waters were calculated through correlation analyses of log-normalised data (Table 4-7). A significant ($p<0.01$) negative correlation was produced by Zn and pH values in the November 2004 road runoff water samples (R^2 = - 0.53). Negative relationships between aqueous concentrations of the other heavy metals and pH values were also evident, but were not statistically significant at the $p<0.01$ or $p<0.05$ interval (Table 4-7).

Table 4-7: Correlation coefficients between pH values and Cd, Cu, Pb, Ni and Zn concentrations in filtered road runoff waters collected from the Kuranda Range Road and the Captain Cook Highway roundabouts in November 2004 (n = 13) and January 2004 (n = 8). Correlation coefficients were calculated using log-normalised data.

	R^2 values			
	Cu and pH	*Pb and pH*	*Ni and pH*	*Zn and pH*
November 2004	- 0.18	- 0.03	- 0.13	- 0.53
January 2004	0	+ 0.09	- 0.04	- 0.07

Notes: Type of correlation is indicated by +/- symbol
Correlation is significant at the $p<0.01$ level

In contrast, the relationships between aqueous heavy metal concentrations and pH values in the road runoff water samples collected in January 2004 were much weaker (Table 4-7). None of these correlations were significant at the $p<0.01$ or $p<0.05$ interval (R^2 = 0 for Cu, R^2 = + 0.09 for Pb, R^2 = - 0.04 for Ni and R^2 = - 0.07 for Zn). This is likely due to the dilution of metal concentrations in these waters by extended periods of rainfall leading up to January 2004 (Table 4-7).

It was noted that the pH values of most of the road runoff water samples collected in this study were in the near-neutral range. This indicated that some component of the road sediments or the road surface itself was responsible for increasing the pH values of these runoff waters from slightly acid to neutral and even moderately alkaline levels. It is well-documented that the pH of pure rainwater is mildly acid due to the presence of carbonic acid (Faure 1991; White 1997). Rainwater samples analysed by this study were also slightly acid (pH <6) (Table 4-1). Despite this, previous research has documented the pH of road runoff waters in the near-neutral range. For example, Rose et al. (2001) recorded a mean pH of 6.49 for urban storm runoff in the city of Atlanta. Sansalone and Buchberger (1997) also found the pH of their studied road runoff water samples to increase from slightly acid levels to near-neutral values during rainfall events (Table 4-8).

Table 4-8: pH values in road runoff waters at the beginning and end of a number of rainfall events in Cincinnati, USA (from Sansalone and Buchberger 1997).

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The results of Sansalone and Buchberger (1997) clearly indicated temporal increases in road runoff water pH values for a number of rainfall events. Causes for these increases in pH were attributed to the road asphalt surface rather than the chemistry of the road sediments (Sansalone and Buchberger 1997). In fact, Sansalone and Buchberger (1997) suggested that the neutralising capacity of asphalt is insufficient to buffer the pH of extremely acid rainfall, despite their results signifying that the pH of road runoff waters was effectively buffered (Table 4-8). An alternative hypothesis is that the frequently observed neutralisation of slightly acid road runoff waters may be caused by road sediments rather than road surfaces.

For example, Serrano-Belles and Leharne (1997) suggested that the carbonate content of road dusts is an effective buffering agent for acidic waters.

However, their work showed that the buffering capacity of the road sediments was eventually overcome with the continuation of addition of acid (Serrano-Belles and Leharne 1997). The carbonate content road sediments collected in this study, particularly those from the Kuranda Range Road, was lower (approximately 3 wt %, Table 3-3 in Chapter 3) than the value recorded in road dusts by Serrano-Belles and Leharne (1997) (ca. 11 wt %). Still, this carbonate may have buffered the pH of studied road runoff waters to near-neutral values.

Serrano-Belles and Leharne (1997) and Sansalone and Buchberger (1997) pointed to buffering of road runoff waters to near-neutral levels, yet both investigations concluded that the buffering capacity of road sediments and road surfaces was limited and ineffective for persistently acid rainfall. However, in this investigation and in the study by Sansalone and Buchberger (1997), the pH levels of road runoff waters remained in the near-neutral range; even following prolonged periods of rainfall. Thus, some factor other than road surfaces and carbonate content of road sediments is likely responsible for consistently maintaining near-neutral pH levels in road runoff waters. Tyre rubber shreds have been suggested to be capable of neutralising soil pore water pH values from slightly acid levels (Smolders and Degryse 2002). In this study, the pH values of the distilled water samples ponded with shredded tyre were found to increase over time (Figure 4-16). Moreover, tyre rubber shreds were shown to dominate the matrix of the road sediment samples (Chapter 3). Therefore, these tyre particles are potential contributors to neutralising the pH of road runoff waters. The specific mechanisms by which tyre rubber particles increase the pH of road sediment leachates and road runoff waters are not known. However, the continual buffering of these waters over prolonged periods suggests that tyre rubber exerts an important control on the pH of road runoff waters. This, in turn, affects the solubility of heavy metals associated with these sediments.

In summary, data from this study have shown that ‘first flush’ waters which exhibit high pH values accommodate lower dissolved aqueous metal values than low-pH waters. The high-pH waters likely favour the adsorption of dissolved metal species onto particulate phases, which has been demonstrated in previous research (e.g. Rose et al. 2000). Following the onset of the ‘wet season’, metal values in road runoff waters are much lower and no discernable relationship is evident between pH and dissolved metal concentrations. Finally, the near-neutral pH of road runoff waters may assist in the adsorption of dissolved metal species. Tyre rubber shreds potentially buffer the road runoff water pH from mildly acid to near-neutral values.

4.4.1.5 Significance of EC in road runoff water samples

Associations between aqueous metal and EC values may provide a useful tool to characterise the chemistry of road runoff waters (Herngren et al. 2005). Herngren et al. (2005) note that "the relationships between heavy metals and parameters such as rainfall pH and EC could also have a significant influence on urban stormwater quality at certain sites".

In this study, the road runoff water samples collected in November 2004 exhibited higher metal concentrations and EC values than the samples taken in January 2004. Correlation analyses indicated that aqueous metal concentrations and EC values in these 'first flush' waters acquired in November 2004 were positively related (Table 4-9). The strength of the correlations were variable for the different metals (Table 4-9). Correlation coefficient (R^2) values between metal concentrations and EC values were: + 0.37 for Cu, + 0.22 for Pb, + 0.48 for Ni and + 0.13 for Zn (Table 4-9). Moreover, Cu and Ni levels were significantly correlated with EC values in the November 2004 road runoff water samples ($p<0.05$ for Cu and $p<0.01$ for Ni) (Table 4-9).

Table 4-9: Correlation coefficients between EC values and Cd, Cu, Pb, Ni and Zn concentrations in filtered road runoff waters collected from the Kuranda Range Road and the Captain Cook Highway roundabouts in November 2004 (n = 13) and January 2004 (n = 8). Correlation coefficients were calculated using log-normalised data.

	R^2 values			
	Cu and EC	*Pb and EC*	*Ni and EC*	*Zn and EC*
November 2004	+ 0.37	+ 0.22	+ 0.48	+ 0.13
January 2004	0	+ 0.24	- 0.07	- 0.06

Notes: Type of correlation is indicated by +/- symbol
Correlation is significant at the $p<0.05$ level
Correlation is significant at the $p<0.01$ level

However, for the road runoff waters collected in January 2004, aqueous metal concentrations and EC values showed no discernable relationships (R^2 = 0 for Cu, + 0.24 for Pb, - 0.07 for Ni and - 0.06 for Zn) (Table 4-9). These varying trends between the January 2004 samples and the November 2004 samples were likely due to the removal of metals and other ions from the road surface at the peak of the 'wet season'. Consequently, runoff waters that flush over road surfaces following heavy rain display a similar chemistry to pure rainwater (i.e. they have low aqueous metal concentrations and low EC values).

4.4.2 Laboratory experiments

4.4.2.1 Column leach experiments

Results from the column leach experiments established road sediments as the likely principal source of the heavy metals detected in the road runoff waters. Cadmium and Zn were shown to be the most soluble of the analysed heavy metals, while Pb was observed to be the least soluble metal in the leachate waters (Section 4.3.4.1). These findings were commensurate with results of other studies (e.g. Sansalone and Buchberger 1997; Dierkes and Geiger 1999).

Elevated aqueous Al, Ca, Cd, Cu, Fe, Pb, Ni and Zn concentrations were detected primarily in the first few volumes of leachate collected from the column containing the Kuranda Range Road sediments (Figure 4-1), conforming to the 'first flush' principal originally defined by Schueler (1987). A similar 'first flush' effect was also observed for the aqueous concentrations of these metals in leachates of the Captain Cook Highway roundabout sediments, although the effect was more subdued (Figure 4-5).

A 'first flush' pattern is expected for all mobile elements under static equilibrium conditions (Figure 4-19a). Only in cases where kinetic dissolution occurs, would it be anticipated that metals be continuously liberated from particle surfaces into the leachates (Figure 4-19b). Under such circumstances, aqueous metal concentrations would not show a 'first flush' pattern in the leachates. Kinetic conditions may account for the weak 'first flush' trend observed for total

Cd, Pb, Al and Fe concentrations in the Captain Cook Highway roundabout leachates.

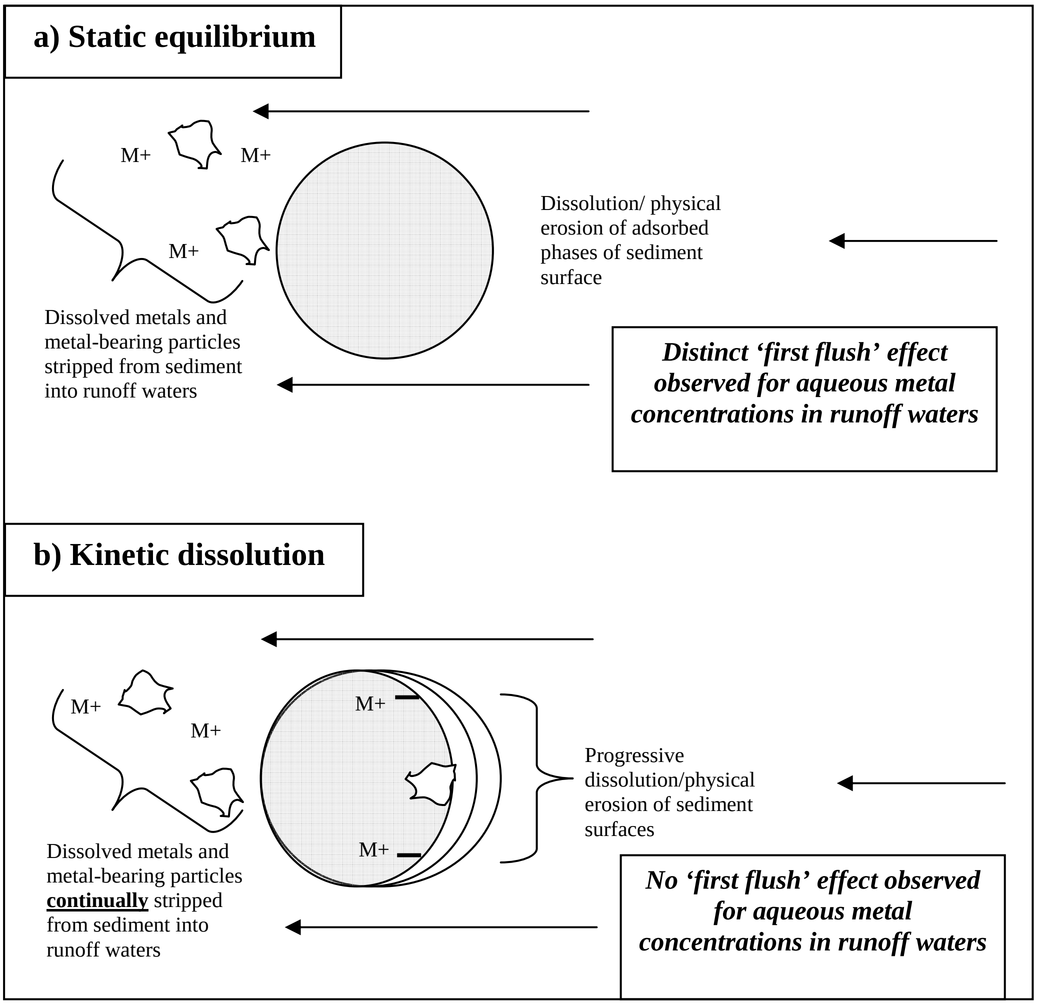

Figure 4-19: Schematic diagram of: a) static equilibrium leading to 'first flush' effect; and b) kinetic dissolution resulting in the absence of a 'first flush' effect for aqueous metal concentrations.

The kinetic release of Cd, Pb, Al and Fe in the Captain Cook Highway roundabout sediment leachates may be explained by the physical flow paths of the waters that passed through this column. It was noted during the experiment that the sediments from the Captain Cook Highway roundabouts formed a more permeable layer than the Kuranda Range Road sediments in the column tubing. Moreover, visual observation confirmed that the first few water volumes poured through the Captain Cook Highway roundabout sediments did not effectively interact with the total sediment reservoir. This may explain why a distinctive ‘first flush’ effect was not observed for total Cd, Pb, Al and Fe concentrations in the leachates from the Captain Cook Highway roundabout sediments. This result is important because it reflects in-situ flow conditions that would be expected to occur in roadside environments.

Comparisons between metal concentrations in filtered and unfiltered leachates indicated that Cd, Cu, Ni, Zn and Ca were mainly present as readily soluble or complexed phases. In contrast, total aqueous Pb, Al and Fe concentrations far exceeded their respective concentrations in the filtered samples, suggesting that these metals were predominantly associated with suspended particulate matter or complexes > 0.45 µm.

Calcium concentrations in filtered samples were consistently commensurate with Ca levels in unfiltered samples in the leachate waters from both columns. Thus, it is likely that Ca was derived from a readily soluble carbonate phase in these road sediments; most likely calcite. As mentioned in Section 4.4.1.4, calcite is a potential source of alkalinity in road sediments. However, the aqueous Ca concentrations in the leachate samples rapidly declined after the second volume of water leached through these columns. This implies that the pH buffering capacity of the soluble Ca compound present in the sediments was extremely limited and exhausted quite rapidly.

In summary, results of the column leach experiments have shown road sediments to be a principal source of soluble metals on road surfaces. The distinctive ‘first flush’ patterns observed for metal concentrations in the leachates have important ramifications for wet-dry tropical locations. The trends suggest that road runoff waters occurring at the onset of the ‘wet season’ are likely to be laden with exceptionally high metal concentrations relative to subsequent runoff waters. This finding supports the conclusions of the road runoff water analyses. Thus, the ‘first flush’ concept for metal contaminant dispersal defined by Schueler (1987) has been demonstrated to be particularly relevant for roadside metal dispersion in wet-dry tropical locations. Road surfaces in these regions experience episodic pulses of flushing which are able to mobilise high concentrations of metal contaminants into adjoining environments.

4.4.2.2 Ponding experiments

The ponding experiments differed from the column leach experiments in that the dissolved oxygen (DO) and the Eh levels in these pond waters decreased over time (Figure 4-11, 4-14). As was the case with the column leach experiments, the pH values of the pond samples steadily increased over the course of the ponding tests (Figure 4-11, 4-14).

Increases in aqueous metal concentrations were observed in the first few samples obtained from the ponded waters (Figure 4-9, 4-12). In fact, an increase in aqueous Cd, Cu and Fe concentrations was recorded in the pond decant samples of the Kuranda Range Road sediments after a period of 1 month of ponding had elapsed (Figure 4-9). Hence, the ponding experiment with the Captain Cook Highway roundabout sediments was conducted over a longer time period to observe if there was any reduction in these metal concentrations in the ponded waters over time. Results from the 3 month ponding experiment conducted on the Captain Cook Highway roundabout sediments suggested that Pb, Fe and Ca were continually released from the sediments into the overlying waters (Figure 4-12). Their liberation into the pond decant waters reflected the kinetic model shown in Figure 4-19b.

The concentration of metals in solution in the studied ponded waters was likely controlled by changes in aqueous chemical conditions. It is known that the aqueous mobility of metals in surficial environments is largely influenced by alterations in Eh-pH conditions (Lee et al. 1997). It may be stated generally that, in cases where metal-hosting sediments are overlain by relatively still waters, metals will be most readily soluble in low pH/high Eh (oxic) waters (Faure 1991) and least soluble or most tightly bound with the sediments in high pH/low Eh (anoxic) waters (Clark et al. 1998). The importance of oxidation-reduction potential and pH in changes to the partitioning of heavy metals in anoxic ponded water bodies has been noted by a number of researchers (e.g. Saeki et al. 1993; Cantwell et al. 2002; Caetano et al. 2003). Specific mechanisms by which changes in these chemical parameters (pH, DO and Eh) affect metal partitioning between sediment surfaces and overlying waters depend on local chemical and biological conditions as well as the composition of the sediments which host the metals (Lee et al. 1997).

The ponding tests performed in this study revealed that the water ponded with the sediments exhibited a range of pH-Eh values. The chemistry of the ponded water bodies gradually shifted from acid and oxic to alkaline and anoxic conditions. It was over this change that general decreases in aqueous metal concentrations in the pond decant samples were observed. Initial increases in metal concentrations recorded in the pond decant samples were likely a result of the desorption or dissolution of those particles that are least stable under strongly oxidising conditions (e.g. salts and fractions weakly adsorbed to host particles). With the introduction of increasingly anoxic conditions in the system, the heavy metals associated with the oxide/oxyhydroxide fraction were likely liberated into the overlying ponded water. The release of metals due to the destruction of oxides under anoxic conditions has been previously documented in ponded water bodies (Parker and Rae 1998).

With the continuation of the ponding experiment (5 weeks and onwards), concentration decreases for most metals were observed (Pb and Ca were exceptions). It is plausible that after this prolonged ponding: a) most of the soluble and readily mobile portion of metals hosted by the sediments had been exhausted by the prior decanted samples (noting that the experiment was a sequential study rather than a batch test); and b) any remaining metals liberated from the destruction of the oxide/oxyhydroxide fraction of the sediments were scavenged by those components that are stable under anoxic conditions (likely organic matter, including the reactive surfaces of tyre rubber shreds). Organic matter has been reported as a principal scavenging agent for aqueous metals under anoxic conditions (Tada and Suzuki 1982).

Overall, results of the ponding experiments suggest that water bodies which stagnate with road sediments have the capacity to limit the release of metals. In wet-dry tropical locations, water bodies may pond with road sediments for prolonged periods of time during the ‘dry season’. It is envisaged that metals in these water bodies are eventually sequestered by adsorbent particles that are stable under anoxic conditions. Alternatively, metals may precipitate out from the stagnant waters during evaporation in the hot temperatures of the tropics. In either case, road sediments that are ponded with stagnant water bodies in wet-dry tropical locations represent a significant repository for metal contaminants.

4.4.2.3 Tyre rubber ponding experiments

Results from the tyre shred ponding experiments suggested that, of the heavy metals analysed, Zn was released in the highest proportions from the surface of the rubber particles into near-neutral pH waters (Figure 4-15). Apart from recording higher concentrations in the tyre pond samples than any of the other metals, Zn was unique in that its concentrations in the pond waters increased over time, even up to the last sample collected after 1 month of ponding.

Results from the two tyre rubber (car and truck) experiments were similar; the exception being that higher metal concentrations were present in the water ponded with the car tyre rubber (Figure 4-15). This was perhaps due to the coarser nature of the truck tyre rubber particles. The smaller size the of car tyre rubber particles would have provided a greater surface area for these particles to react with the pond water.

Previous research has shown that Zn associated with tyre particles is soluble in soil pore waters. For example, a study by Smolders and Degryse (2002) revealed that Zn was released from shredded car and truck tyre particles mixed with soils, with elevated Zn concentrations detected in soil pore waters and soil leachate waters in their extended study (over 1 year). The amount of Zn present in the soil pore waters appeared to be dependent on the chemical characteristics within the waters (Eh-pH) and at the soil/water boundary (Smolders and Degryse 2002).

By comparison, this study constitutes the first examination of Zn solubility in pond waters. The Zn liberated from the tyres is likely derived from a zinc-oxide coating spray. The average ZnO concentration in tyres is approximately 2 wt % (Amari et al. 2000). Commonly, this zinc oxide compound is considered unreactive in surficial environments (Amari et al. 2000). However, the results of this study suggested that this Zn compound was readily soluble over time. It is hypothesised that the observed decreases in Eh values over the experiment represent a potential cause for the continual release of Zn into the ponded waters. The ZnO coating compound on these tyre shreds may have become increasingly unstable under anoxic conditions.

In summary, the experiments demonstrated that tyre shreds represent a significant source of water-soluble Zn. Moreover, Zn is clearly continuously released into solution despite slight pH increases brought about by the buffering capacity of tyre rubber shreds.

4.5 Conclusions

Road runoff waters on the Kuranda Range Road and the Captain Cook Highway roundabouts were shown to transport dissolved (<0.45 µm) and particulate metals (>0.45 µm). Median Cu, Pb and Zn values in filtered (<0.45 µm) road runoff waters acquired from the Kuranda Range Road during an early 'wet season' rainfall event in November 2004 were: 17x, 25x and 15x higher than their background levels. In comparison, Cu and Zn values in samples acquired during February 2003 and January 2004, after periods of heavy rainfall, were strongly diluted relative to the November 2004 samples. Despite this, median Cu, Pb and Zn concentrations in the road runoff waters sampled in February 2003 and January 2004 were still elevated (Cu 8x, Pb 27x and Zn 9x) above baseline levels (as determined by values in the stream samples). This finding highlights the persistent presence of these metals on road edges even after flushing by heavy rain.

The pH values of the studied road runoff water samples were in the near-neutral range. This near-neutral pH likely limits the solubility of most heavy metals in road runoff waters. Despite this, Zn was found to relatively soluble in the road runoff waters analysed in this study.

Analyses of road sediment leachates from the column experiments revealed that aqueous concentrations of most of the studied metals exhibited a strong 'first flush' effect. Furthermore, the majority of the metals present in the leachates were readily soluble (as determined by 0.45 µm filtrate) indicating that these metals would be expected to be particularly mobile in road runoff waters.

The sequential ponding experiments demonstrated that metals were slowly but continuously released from road sediments into pond waters under increasingly anoxic conditions, despite a corresponding rise in pH; which was likely induced by the presence of tyre rubber particles. These metal concentrations in the pond decant waters then gradually decreased as the soluble and readily mobile supply of metals were exhausted from the road sediments under increasingly anoxic and alkaline conditions. These anoxic conditions presumably favoured the scavenging of any remaining dissolved or colloidal metals onto organic matter, including tyre rubber particle surfaces.

Tyre rubber was confirmed as a significant contributor of soluble Zn in road runoff waters. The ZnO coating on tyre rubber is a likely source of Zn. In roadside environments, the solubility of Zn released from tyre rubber particles by road runoff waters will be controlled by the scavenging potential of underlying sediments.

In summary, road runoff waters at the onset of the ‘wet season’ in tropical environments exhibit elevated metal concentrations. These metals are derived from soluble and fine-grained particulate metal phases that accumulate on road surfaces during the prolonged ‘dry season’. Consequently, ‘first flush’ road runoff waters potentially deliver high metal concentrations into nearby soils and streams. After the commencement of the ‘wet season’, road runoff water metal values decrease considerably and the output of metal contaminants to adjoining environments is thereby diminished.

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Chapter 5 Heavy metal and PGE concentrations in stream sediments: Pb isotopes and PGE enrichment as indicators of traffic contamination

5.1 Introduction

Stream sediments are one of the sinks for traffic-derived metals (Sutherland 2000; Zereini and Alt 2000; Siegel 2002). Within stream waters, dissolved metals may be adsorbed to suspended colloidal material (Bordas and Bourg 2001; Caetano et al. 2003). These colloids consist largely of clays, oxides and organic matter. Once metals are adsorbed onto these particles, their desorption is not readily favoured under normal stream pH and Eh conditions (Parker and Rae 1998). Metal-bearing colloids eventually settle out of solution as they are scavenged by bed sediments (Faure 1991). Consequently, elevated metal concentrations are commonly observed in the basal sediments of water bodies that receive runoff waters affected by polluting activities (Lee et al. 1997).

Generally, the magnitude of contamination within these sediments is best studied through examination of the finer-grained material, where anthropogenic metal loadings are most pronounced compared with background values (Sutherland 2000; Munksgaard and Parry 2002; Simonovski et al. 2003). However, in cases where the effects of anthropogenic sources on heavy metal and PGE concentrations are more subtle, other techniques need to be used to examine the impacts of contamination.

The application of stable Pb (^{204}Pb) and radiogenic Pb isotopes (^{208}Pb, ^{207}Pb, ^{206}Pb) has emerged as a powerful indicator to discriminate various sources of Pb in the environment. Relationships between the Pb isotopes ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb have been widely used to interpret the extent of Pb contamination in atmospheric dusts (Chiaradia et al. 1997), sediments (DeVivo et al. 2001), soils (Gulson et al. 1981), groundwaters (Toner et al. 2003) as well as plant (Tommasini et al. 2000) and even human (Gulson et al. 1994b) tissue.

Since the formation of the Earth, the abundances of the three radiogenic Pb isotopes have been steadily increasing due to the decay of their parent isotopes (^{238}U decays to ^{206}Pb, ^{235}U decays to ^{207}Pb, and ^{232}Th decays to ^{208}Pb), while the abundance of ^{204}Pb at the Earth's surface has remained unchanged (Cumming and Richards 1975). Moreover, Pb deposits have 'locked in' a specific Pb isotopic signature at the time of their formation. Thus, Pb from these orebodies should, in theory, exhibit lower radiogenic Pb/non-radiogenic Pb ratios than soil Pb, due to the lower abundance of the radiogenic Pb isotopes relative to ^{204}Pb at the time of ore formation (Ault et al. 1970). Manufactured Pb in Australia, including Pb in petrol, is predominantly derived from Broken Hill or Mt Isa type deposits. Australian Proterozoic Pb orebodies are commonly characterised by Pb isotopic ratios of $^{208/204}$Pb = 36, $^{206/204\text{Pb}}$ = 16, $^{207/206}$Pb = 0.95 and $^{208/206}$Pb = 2.25 (Gulson et al. 1981).

While the above theory underpins the application of Pb isotopes as environmental markers, there are a number of problems associated with the method. Firstly, the specific Pb isotopic signature of a Pb orebody or a given soil profile does not only depend on their age of formation, but also on the initial U and Th abundance in these geological materials (Gulson et al. 1981; Munksgaard et al. 2003). Secondly, it is difficult to establish the specific signature of anthropogenic-derived Pb in the environment because there may be a number of different sources for this, with each exhibiting its own unique Pb isotopic signature (Elbaz-Poulichet et al. 1986). Another major problem with the technique stems from the imprecision of standard ICP-MS techniques to measure levels of the ^{204}Pb isotope, which has a relatively low abundance. Precise but time-consuming analytical techniques, notably thermal ionisation mass spectrometry (TIMS), are more effectively able to measure levels of the ^{204}Pb isotope (Gulson et al. 1981; Munksgaard et al. 2003).

Another approach to avoid error associated with measuring the uncommon ^{204}Pb isotope has been to focus purely on the ratios of the relatively abundant radiogenic Pb isotopes. There are differences in the rate of formation of the three radiogenic isotopes. The abundance of ^{206}Pb has been increasing with respect to ^{207}Pb and ^{208}Pb (Munksgaard et al. 2003). Consequently, orebody Pb commonly displays relatively high ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios compared with 'background' soil (Munksgaard et al. 2003). Thus, cautious analysis of the three radiogenic Pb isotopes can provide a reasonable indication of anthropogenic Pb in the environment. However, this is not universally true, since it should be borne in mind that the Pb isotopic signature will also depend on the relative abundance of the parent isotopes. In any study, the data provided by Pb isotopes can only be satisfactorily interpreted providing that: a) a rigorous analysis of the Pb isotopic signature of local background environmental media is conducted; and b) the Pb isotopic signature of the source of contamination is known or, at least, reasonably assumed.

This chapter examines the dispersion of heavy metals and PGEs in stream sediments within a catchment system that is intersected by the Kuranda Range Road and the Captain Cook Highway in Cairns. Specifically, the aims are: a) to determine the dispersal of heavy metal and PGE contaminants within stream sediments from Avondale Creek, from its source to its sink in estuarine sediments; and b) to resolve the anthropogenic component of Pb contamination in these sediments through Pb isotope analysis.

This research is unique in that it is the first study in a tropical location to examine metal contamination within a stream system where road and urban runoff can be reasonably appointed as the principal sources of contamination. There are no mining or industrial activities in the area. This study is also the first to investigate the dispersion of traffic-derived metals at the fringe of the Great Barrier Reef lagoon.

5.2 Methods of analysis

Three road sediment samples and twelve stream sediment samples collected from the project area (refer to Appendix A for details) were dried and sieved to less than 75 µm (Chapter 2 – Section 2.4.8). The sediments were analysed for their $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios at CDU, Darwin. Additionally, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios, as well as $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios were determined for the same twelve stream sediments and three different road sediment samples (Appendix A) submitted to ANSTO, Sydney (Chapter 2 – Section 2.4.8).

Further to the above, three stream sediment samples (S9, S21 and S25, Chapter 2 – Section 2.4.3.2) were analysed for their particle-size distribution by a Malvern Mastersizer Laser Particle Size Analyser in Townsville. The same samples were analysed for their C_{org}, $S_{sulfide}$, $S_{sulfate}$ and Fe-Mn oxide/oxyhydroxide contents at the AAC, Townsville and at ALS, Brisbane (S9, S21 and S25, Chapter 2 – Section 2.4.7.1).

5.3 Results

5.3.1 General characteristics of the stream and estuarine sediments

The Avondale Creek catchment investigated in this part of the study has been divided into three main sections, based on a number of characteristics of the stream system. These include distance from the coast and the predominant stream sediment type (Figure 5-1).

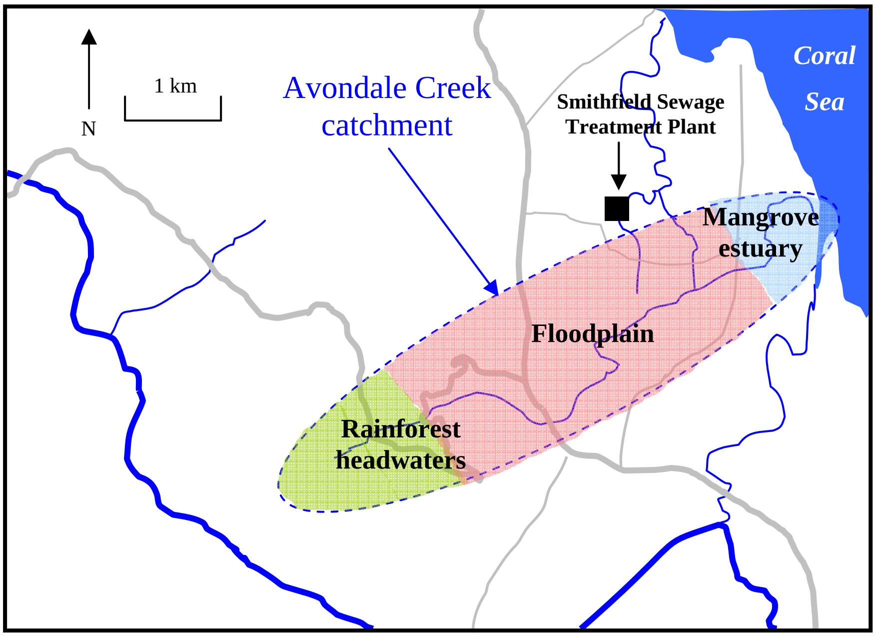

Figure 5-1: Studied sections of the Avondale Creek catchment system.

The stream sediments in the rainforest headwaters section of the catchment varied considerably in grain size. Visual observation of the sediments indicated a range of particle types from coarse-grained weathered rock fragments to very fine-grained, light brown organic particles. Approximately 4 % by volume of the <75 µm fraction of the sediments collected from the headwaters of the stream was determined to be in the <2 µm particle size fraction (Figure 5-2).

By comparison, the sediments collected from the floodplain at the base of the range were generally very fine-grained silts and muds. These ranged in colour from light brown to dark grey/black. The <2 µm particle size fraction constituted ca. 7.5 % by volume of the <75 µm fraction of the sediment collected from the floodplain (Figure 5-2).

Finally, the sediments taken from the mouth of the creek catchment system, in the mangrove estuary, consisted of fine-grained, light grey organic muds interbedded with sands and silts. Nearly 5.5 % by volume of the <75 µm fraction of the sediment collected from the estuary was present in the <2 µm particle size fraction (Figure 5-2).

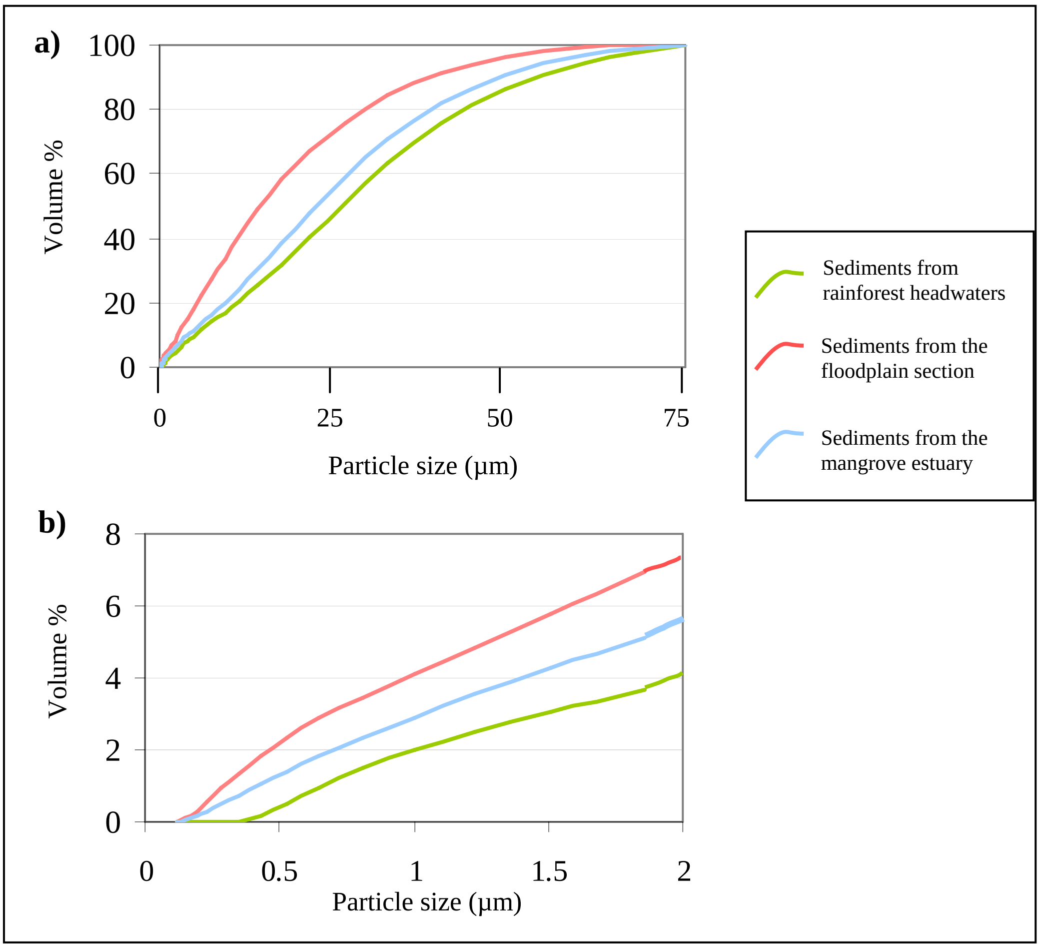

Figure 5-2: Cumulative distribution of particle sizes in a) the <75 µm fraction and b) in the <2 µm fraction of the various sediment types. Refer to Appendix A for sample ID details.

$S_{sulfate}$, $S_{sulfide}$, S_{total}, C_{org}, MnO and Fe_2O_3 values were determined in three sediment samples (S9, S21 and S25, Appendix A) representative of the three sections of the creek system, and the data are shown in Table 5-1. In the rainforest headwaters, sediment $S_{sulfate}$ and $S_{sulfide}$ concentrations were 0.07 wt % and 0.01 wt %, respectively. Additionally, C_{org}, MnO and Fe_2O_3 levels in these sediments were 12.9 wt %, 0.06 wt % and 2.99 wt %, respectively (Table 5-1). By comparison, $S_{sulfate}$ and $S_{sulfide}$ values in the sediments from the floodplain were 0.11 wt % and 0.07 wt %, respectively (Table 5-1). Moreover, these sediments hosted 3.5 wt % C_{org}, 0.13 wt % MnO and 5.67 wt % Fe_2O_3 (Table 5-1). Finally, the estuary sediments contained 0.025 wt % $S_{sulfate}$ and 0.015 wt % $S_{sulfide}$ (Table 5-1). The C_{org}, MnO and Fe_2O_3 levels in these estuarine sediments were 1.9 wt %, 0.11 wt % and 5.38 wt %, respectively (Table 5-1).

Table 5-1: $S_{sulfate}$, $S_{sulfide}$, Total S, C_{org}, MnO and Fe_2O_3 values (wt %) in stream and estuarine sediments (n = 3). Refer to Appendix A for sample ID details and Appendix B for data.

	Sample ID		
	S9 from the rainforest headwaters	***S21 from the floodplain section***	***S25 from the mangrove estuary***
$S_{sulfate}$ (wt %)	0.07	0.11	0.025
$S_{sulfide}$ (wt %)	0.01	0.07	0.015
S_{total} (wt %)	0.08	0.18	0.04
C_{org} (wt %)	12.9	3.5	1.9
Total Mn as MnO (wt %)	0.06	0.13	0.11
Total Fe as Fe_2O_3 (wt %)	2.99	5.67	5.38

5.3.2 Total heavy metal and PGE concentrations in stream sediments

Total heavy metal and PGE concentrations in the <75 μm fraction of the stream sediments collected from Avondale Creek showed variable patterns (Figure 5-3). Cadmium concentrations steadily decreased in the stream sediments from the rainforest headwaters down to the estuary at Yorkeys Knob (Figure 5-3). By comparison, sediment Cu values were relatively constant from the rainforest headwaters to the estuary, whilst Ni concentrations were considerably higher in the rainforest headwater sediments than in the stream sediments collected downstream of the roads (Figure 5-3). In contrast, stream sediment Pb levels steadily increased down the course of the catchment (Figure 5-3). Zinc concentrations exhibited a slight increase from the rainforest headwater stream sediments to the floodplain sediments (Figure 5-3). However, within the estuarine sediments, a sharp rise in Zn concentrations was observed (Figure 5-3).

Furthermore, it was noted that Pd concentrations increased very slightly in the stream sediment samples from the rainforest headwaters to the estuary (Figure 5-3). By comparison, Pt values were distinctly elevated in the estuarine sediment when compared with the rainforest headwater stream sediment (Figure 5-3).

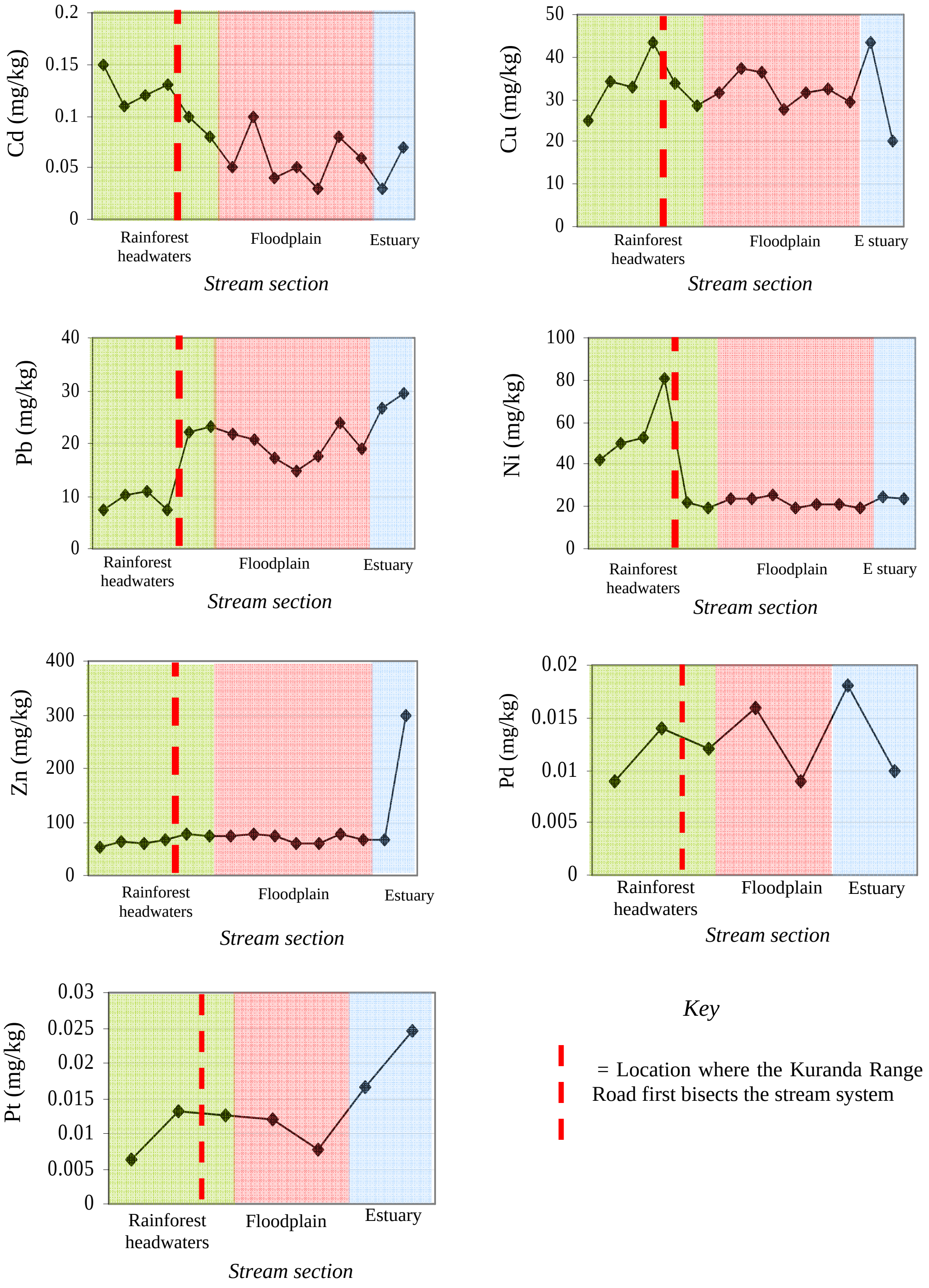

Figure 5-3: Total heavy metal and PGE concentrations in stream sediments (<75 µm) from various sections of the Avondale Creek catchment. Sample location details were shown in Chapter 2 – Section 2.4.1. Sample ID details are presented in Appendix A and data are given in Appendix B.

5.3.3 Sediment Pb isotope geochemistry

For the results of the Pb isotope analysis, the stream sediment samples were placed in two groups: a) those collected upstream of the location where Avondale Creek is first crossed by a road (i.e. the Kuranda Range Road at an elevation of approximately 320 m AHD); and b) those acquired downstream of this road intersection. This distinction was made in order to investigate the impact of the first road crossing on the Pb distribution in stream sediments within Avondale Creek. It is important to note that a number of sediment samples collected from the section of Avondale Creek referred to as the 'rainforest headwaters' (Figure 5-1) were taken downstream of the first road intersection. The estuarine sediment samples are still reported in a separate group to the floodplain sediments; in order to explore whether there is any magnification of anthropogenic Pb within sediment at the mouth of the catchment.

5.3.3.1 Pb isotopic ratios

Three road sediment and twelve stream and estuarine sediment samples were analysed for their ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios at CDU and the data are plotted in Figure 5-4. The ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios of the three road sediment samples analysed by CDU were less radiogenic than those derived for the estuarine sediments (Figure 5-4). There were no discernable differences in these Pb isotopic ratios between the stream sediments collected upstream of the first road crossing, and the samples taken further downstream (Figure 5-4).

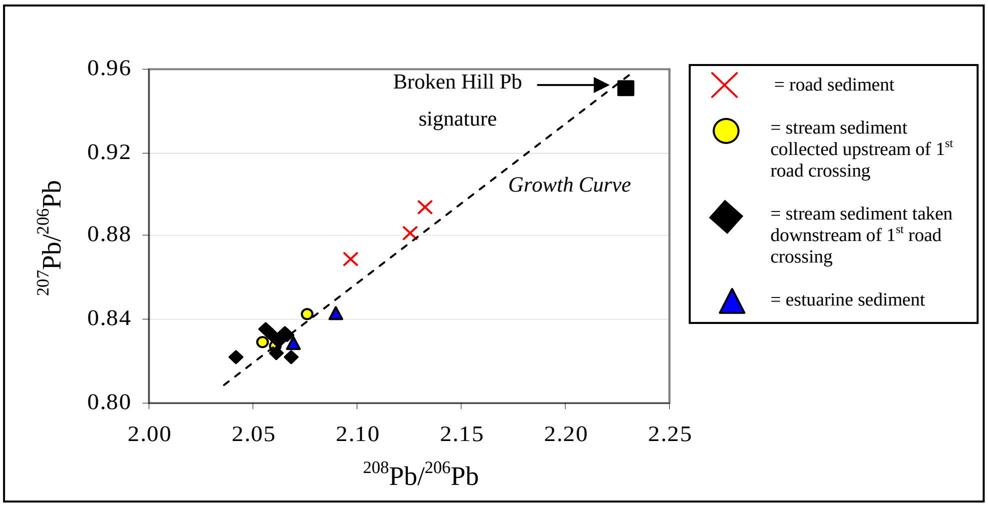

Figure 5-4: $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ ratios for sediments (<75 µm) collected from the Avondale Creek catchment, analysed by CDU. Growth Curve, Broken Hill signature from Gulson et al. (1981). For the road sediment, n = 3; estuarine sediment, n = 2; stream sediment collected upstream of the 1st road crossing, n = 3; stream sediment taken downstream of the 1st road crossing, n = 7. Sample processing was described in Chapter 2 – Section 2.4.8. Sample ID details are presented in Appendix A and data are given in Appendix B.

The exact same twelve stream and estuarine sediments that were submitted to CDU, were analysed for their $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios at ANSTO. Similar $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios to those given by CDU were observed for the same sediment samples analysed by ANSTO (Figure 5-5). Results from this particular analysis, however, showed that the stream sediments collected upstream of the location where Avondale Creek first encounters the Kuranda Range Road, displayed a more radiogenic Pb isotopic signature compared with the downstream sediments (Figure 5-5). Moreover, the estuarine material exhibited a less radiogenic Pb isotopic signature than the other stream sediment samples (Figure 5-5). It should be noted that the ANSTO data plot marginally above the Broken Hill growth curve and this is very unusual for Australian soils or sediments. This is likely attributable to bias incorrection in the laboratory's analytical technique. However, the data may still be used to discriminate radiogenic from non-radiogenic Pb in the studied sediments as all data points lie on the same growth curve as one another.

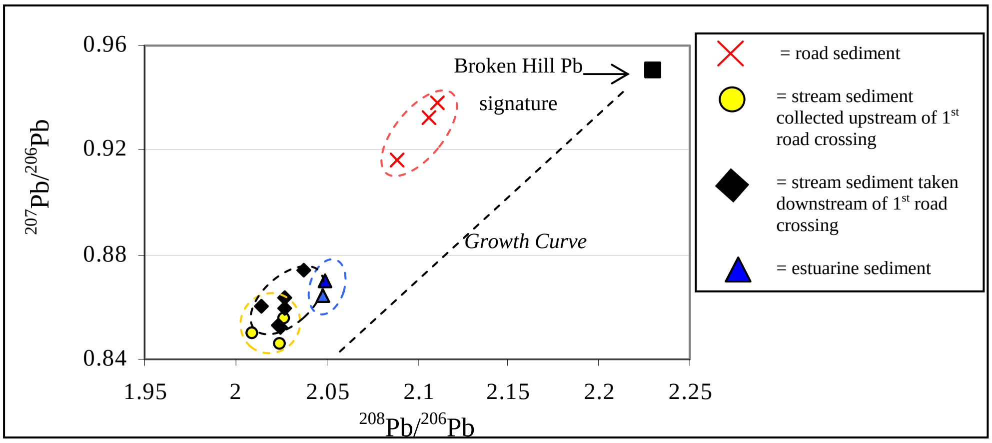

Figure 5-5: ^{207}Pb/^{206}Pb vs. ^{208}Pb/^{206}Pb ratios for sediments (<75 μm) collected from the Avondale Creek catchment, analysed by ANSTO. Growth Curve, Broken Hill signature from Gulson et al. (1981). For the road sediment, n = 3; estuarine sediment, n = 2; stream sediment collected upstream of the 1st road crossing, n = 3; stream sediment taken downstream of the 1st road crossing, n = 7. Sample processing described in Chapter 2 – Section 2.4.8. Sample ID; Appendix A, data; Appendix B.

Analyses of the ^{204}Pb isotope were also performed by ANSTO and the ratios of this isotope with the radiogenic Pb isotopes are shown in Figure 5-6. The ^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios plotted well below the Broken Hill growth curve (Gulson et al. 1981). The three road sediment samples displayed non-radiogenic ^{208}Pb/^{204}Pb signatures which were even less radiogenic than that of the Broken Hill deposit (Figure 5-6).

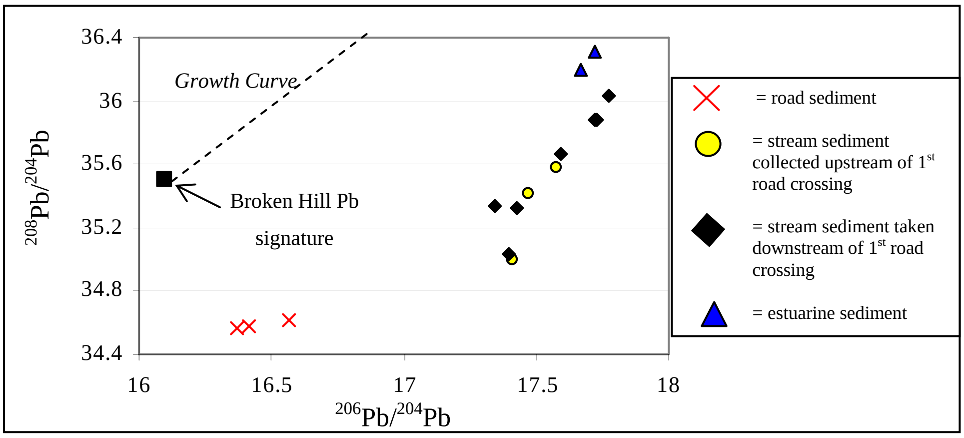

Figure 5-6: ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb ratios for sediments (<75 μm) collected from Avondale Creek, analysed by ANSTO. Growth Curve, Broken Hill signature from Gulson et al. (1981). For the road sediment, n = 3; estuarine sediment, n = 2; stream sediment collected upstream of the 1st road crossing, n = 3; stream sediment taken downstream of the 1st road crossing, n = 7. Sample processing described in Chapter 2 – Section 2.4.8. Sample ID; Appendix A, data; Appendix B.

Total Pb values were also measured in the stream and estuary sediment samples analysed by CDU, and the data are presented in Figure 5-7. Total Pb concentrations in the stream sediments collected prior to the first road crossing were much lower than sediment Pb levels downstream (Figure 5-7). Moreover, total Pb levels observed in the estuarine sediment remained elevated above the Pb values in the sediments acquired upstream of the first road crossing (Figure 5-7).

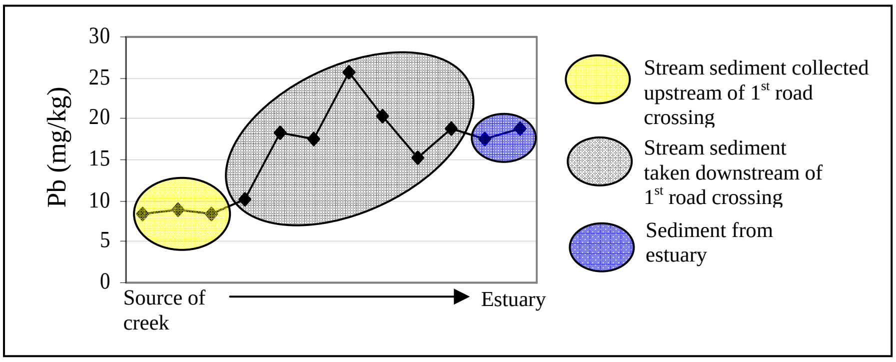

Figure 5-7: Total Pb concentrations in stream sediment (<75 µm) from background locations (upstream of all roads) to the mangrove estuary. Sediments analysed by CDU. Sample processing was described in Chapter 2 – Section 2.4.8. Sample ID details are presented in Appendix A and data are given in Appendix B.

Generally, stream sediment samples collected upstream of the first road intersection exhibited low total Pb values but variable $^{207/206}$Pb and $^{208/206}$Pb ratios (Figure 5-8). In comparison, the sediment downstream of the initial road intersection (including the estuarine sediment) displayed higher total Pb concentrations, although still showed variable $^{207/206}$Pb and $^{208/206}$Pb ratios (Figure 5-8).

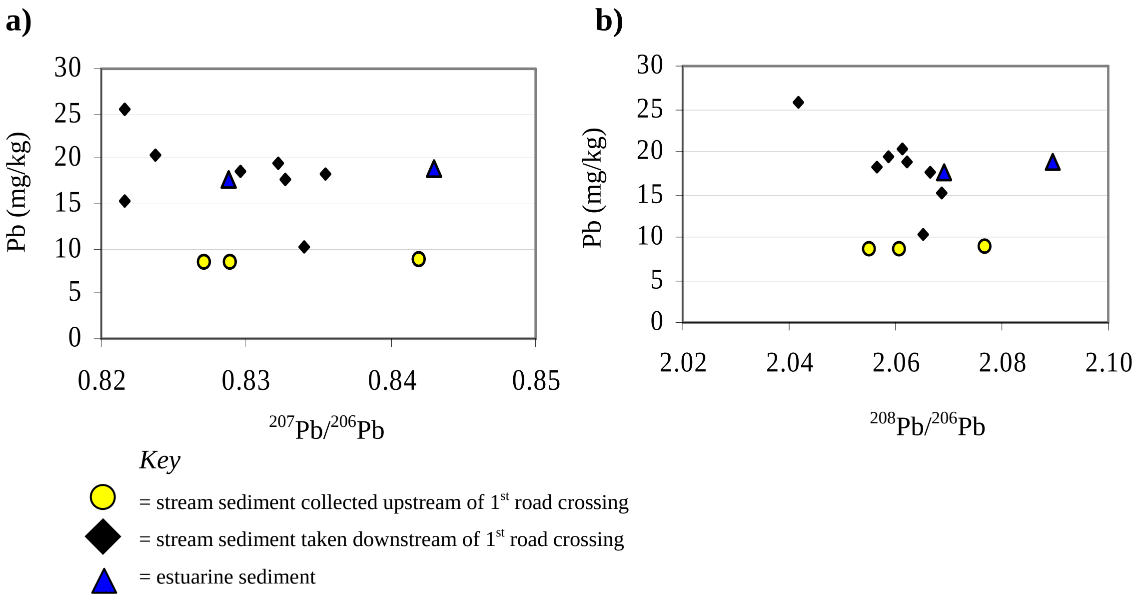

Figure 5-8: a) $^{207/206}$Pb vs. total Pb; and b) $^{208/206}$Pb vs. total Pb in stream and estuarine sediment, <75 µm, analysed by CDU. Sample processing was described in Chapter 2 – Section 2.4.8. Sample ID details are presented in Appendix A and data are given in Appendix B.

Total Pb values in the stream and estuarine sediments analysed by ANSTO were also measured, and the values are presented in Figure 5-9. The total Pb concentration trends were similar to the CDU data (Figure 5-9). Total Pb concentrations were lowest in the stream sediment specimens taken upstream of the point where the Kuranda Range Road first crosses Avondale Creek (Figure 5-9).

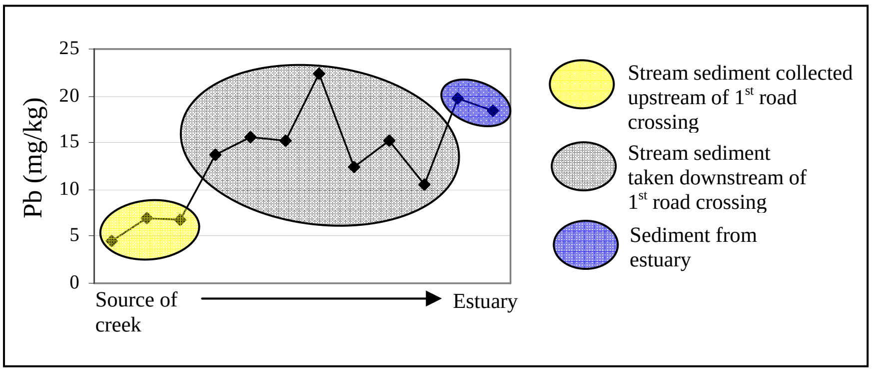

Figure 5-9: Total Pb concentrations in stream sediment (<75 µm) from background locations (upstream of all roads) to the estuary, sediment analysed by ANSTO. Sample processing was described in Chapter 2 – Section 2.4.8. Sample ID details are presented in Appendix A and data are given in Appendix B.

Results of the ANSTO analyses revealed that stream sediments acquired upstream of the first road intersection exhibited low total Pb values and low $^{207/206}$Pb and $^{208/206}$Pb ratios compared with the stream and estuarine sediment samples collected downstream of the road crossing (Figure 5-10). Moreover, the estuarine material displayed consistently high $^{207/206}$Pb and $^{208/206}$Pb ratios and total Pb concentrations (Figure 5-10).

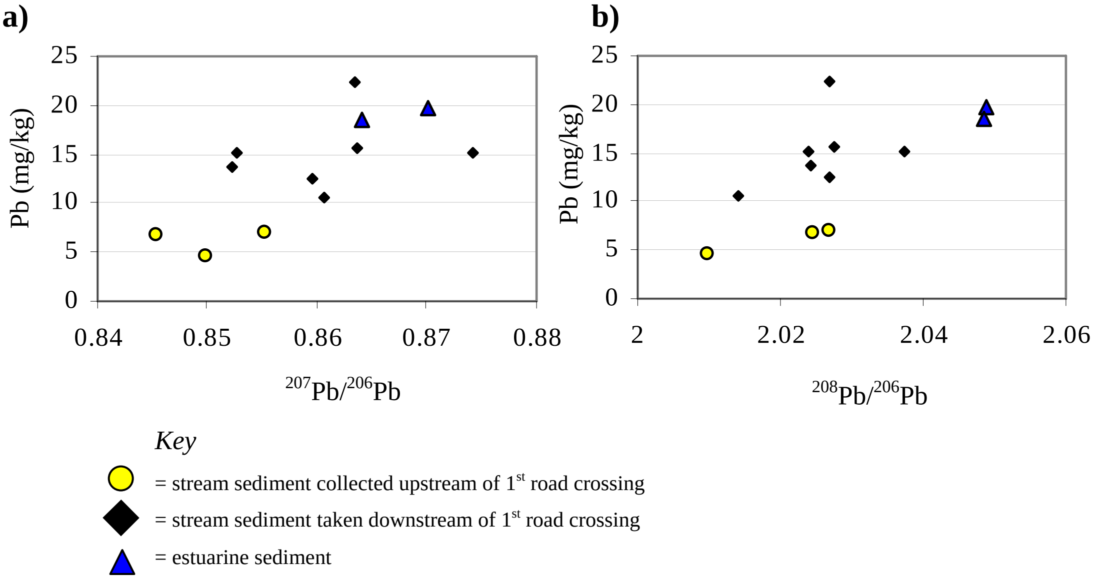

Figure 5-10: a) $^{207/206}$Pb vs. total Pb; and b) $^{208/206}$Pb vs. total Pb in stream and estuarine sediment, <75 µm, analysed by ANSTO. Sample processing was described in Chapter 2 – Section 2.4.8. Sample ID details are presented in Appendix A and data are given in Appendix B.

5.4 Discussion

5.4.1 Total metal concentration data

The stream and estuary sediment metal concentrations detected in Avondale Creek were compared with values documented by other studies that have examined the metal distribution in fluvial sediments of urban landscapes around the world. The comparative data are presented in Table 5-2.

Concentrations of Cd, Cu and Pb in the stream sediments analysed in this study were much lower than those levels reported for other urban streams (Table

5-2). However, data in Table 5-2 show that Ni and Zn values in fluvial sediment taken from other locations were commensurate with the Ni and Zn concentrations of the studied sediments from Avondale Creek. Moreover, Pd and Pt concentrations recorded in the stream and estuarine sediments in this investigation were much higher than their levels reported in stream sediments examined within an industrial area in England by deVos et al. (2003) (Table 5-2).

The stream sediment metal values determined in Avondale Creek were also assessed against ANZECC ISQG Draft Guidelines (Australian Department of Environment and Heritage 2000a) as well as average crustal metal values (Table 5-2). The metal values detected in the stream sediments in this study were all below the low trigger ISQG stipulated by ANZECC (2000), with the exception of Ni (Table 5-2). Nickel levels were above the low trigger but below the high trigger ISQG (2000) in the sediments from the rainforest headwaters, the floodplain and the estuary of the Avondale Creek catchment system (Table 5-2).

Compared with average crustal values, Cd, Cu and Ni concentrations were low in the sediment collected from all sections of the Avondale Creek catchment system (Table 5-2). However, stream sediment Pb levels were commensurate with average crustal Pb values (Table 5-2). Moreover, further downstream the floodplain and estuarine sediments in Avondale Creek exhibited Pb concentrations above average crustal Pb levels (Table 5-2).

The Zn contents of the sediment taken from the rainforest headwaters and the floodplain were in the range of average crustal Zn values (Table 5-2). In contrast, one estuarine sediment displayed a much higher Zn concentration than the average crustal value for this metal (Table 5-2). Finally, concentrations of Pd and Pt were above their average crustal levels in sediment collected from all sections of the stream and estuary (Table 5-2).

Table 5-2: Metal concentrations (mg/kg) in fluvial sediments impacted by urban runoff waters. Concentrations are presented as mean values. L* = Low Trigger values, H* = High Trigger values. NE = None established.

Location	**Sediment type**	**Author**	**Cd**	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**
Taejon Stream, Korea	*Stream*	(Kim et al. 1998)	0.99	151	41.6	-	141	-	-
Hawkesbury River, Australia	*River*	(Simonovski et al. 2003)	-	47	55	-	135	-	-
Rio De La Plata, Argentina	*Stream*	(Ronco et al. 2001)	<0.5	28.7	34.4	11.8	86.8	-	-
Oahu, Hawaii, residential	*Stream*	(Sutherland et al. 2000)	0.86	206	84	324	262	-	-
Throsby Creek, Newcastle, Australia	*Estuarine*	(Lottermoser 1998)	2	50	317	49	784	-	-
Volturno River, Italy	*River*	(DeVivo et al. 2001)	0.45	38	30	23	79	-	-
Port Macquarie Area, Australia	*River and estuary*	(Ashley and Napier 2005)	0.11	36	35	143	76	-	-
A256, Kentish Stour, England	*Stream*	(de-Vos et al. 2002)	-	-	-	-	-	0.0021	0.0018
Avondale Creek, rainforest headwaters (n = 6)	*Stream*	This study	0.12	33.2	13.8	44	64.8	0.012	0.010
Avondale Creek, floodplain (n = 7)	*Stream*	This study	0.06	32.7	19.7	22.5	69.7	0.013	0.010
Avondale Creek, estuary (n = 2)	*Estuarine*	This study	0.05	31.5	29	21.3	182.5	0.014	0.021
Recommended Interim Sediment Quality Draft Guidelines (ISQG, 2000)		ANZECC L*	1.5	65	50	21	200	NE	NE
		ANZECC H*	10	270	220	52	410	NE	NE
Average crustal values		(Smith and Huyck 2004)	0.18	60	16	80	70	0.01	0.005

5.4.2 Pb isotopic ratios of the sediments

5.4.2.1 Samples analysed at CDU

Plotted ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb ratios clearly confirm the presence of anthropogenic Pb in the three road sediment samples (Figure 5-4). These particular Pb isotopic ratios for the road sediments plotted in the vicinity of the Pb isotopic signature of the Broken Hill orebody (non radiogenic). Most of the Pb used in manufacture in Australia is derived from the Broken Hill orebody and similar Proterozoic orebodies (e.g. Mount Isa) (Gulson et al. 1981).

The analysis by CDU yielded no obvious difference in ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb ratios between the sediments collected upstream of the first road intersection and the material collected downstream of this juncture (Figure 5-4). However, the estuarine sediment exhibited slightly less radiogenic ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb ratios relative to the other stream sediment samples (Figure 5-4). This implied a subtle but detectable presence of anthropogenic Pb within the estuarine sediment deposits.

5.4.2.2 Samples analysed at ANSTO

The ANSTO analyses showed that the ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb ratios in the road sediments were extremely non-radiogenic relative to the stream and estuarine sediment samples, confirming the presence of anthropogenic Pb (Figure 5-5). Additionally, the sediments collected upstream of the first road crossing clearly displayed a more radiogenic ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb signature compared with the sediments taken downstream (Figure 5-5). This finding provides strong evidence for the presence of anthropogenic Pb in the stream sediment located downstream of the point where Avondale Creek first encounters the Kuranda Range Road. Moreover, the estuarine sediment displayed non-radiogenic ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb ratios relative to the other stream sediment (Figure 5-5). This suggests that anthropogenic Pb is accumulating within the sediment of the Avondale Creek estuary.

A clearer indication of the presence of anthropogenic Pb downstream of the road crossings is given by plotting ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios against total Pb concentrations (Figure 5-10). Non-radiogenic Pb isotopic signatures were evident in the estuarine sediment samples, which also exhibited relatively high total Pb concentrations (Figure 5-10). Conversely, strong radiogenic signatures were observed in the background sediment samples which showed low total Pb levels (Figure 5-10).

Samples submitted to ANSTO were also analysed for ^{204}Pb isotopic ratios in addition to the other radiogenic Pb isotopes. However, plotted ^{206}Pb/^{204}Pb versus ^{208}Pb/^{204}Pb ratios did not provide any clear trends (Figure 5-6). The isotopic ratios of the three road sediment samples were extremely non-radiogenic with respect to ^{208}Pb/^{204}Pb (Figure 5-6). In fact, they were much less radiogenic than the Broken Hill orebody (Chiaradia et al. 1997). The ^{206}Pb/^{204}Pb versus ^{208}Pb/^{204}Pb ratios of the stream and estuarine sediments plotted away from the Broken Hill growth curve (Figure 5-6), which is extremely uncommon for sediments and soils within Australia (Gulson et al. 1981). There are two distinct possibilities that may have caused this. The first possibility is that there was a strong degree of mixing of Pb derived from other anthropogenic sources containing varying concentrations of the U and Th parent isotopes. Not all of the anthropogenic Pb used in Australia is derived from Australian Pb orebodies. For example, Gulson et al. (1981) note that Pb derived from geologically younger North American Pb deposits has also been used in the manufacture of leaded petrol in Australia. The Pb isotopic signatures of American orebodies are strongly variable (Chillrud et al. 2003). The presence of Pb mixed from a number of differing orebody sources within these sediments is, however, unlikely. If there was a strong 'mixed' signature for the ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotopes within the sediments then it would be reasonable to also expect a 'mixed' signature for the ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios. This was not observed as the ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios for all studied sediment samples fitted on a smooth growth curve.

A more likely explanation for the discordant ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios recorded in this study is the imprecision of the ICP-MS technique used to measure the relatively rare ^{204}Pb isotope. The problem of large errors arising in measuring the less abundant ^{204}Pb has been noted by Gulson et al. (1981), especially in using ICP-MS (Munksgaard et al. 2003).

5.4.2.3 Summary of Pb isotopic ratios in the sediments

Overall, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios in the datasets analysed by CDU and ANSTO suggested that Pb contamination was detectable in Avondale Creek, downstream of the Kuranda Range Road. The contamination signature for these particular isotopes was most pronounced in the estuarine sediments.

Variations in results for the same samples analysed by the two analytical centres were subtle, reiterating the need for repeated analyses using different sample digests in order to ensure an effective interpretation for Pb isotopic data. It is likely that the stronger digest (HF-HNO_3-HCl) used by ANSTO yielded a more complete data set of ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios than those determined by CDU (HNO_3-$HClO_4$ digest used). However, the ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb dataset produced by ANSTO was inferred to be marred by poor precision inherent in the analytical instrumentation (ICP-MS).

5.4.3 Potential sources for metal enrichment in the sediments

5.4.3.1 Natural sources

Caution must be exercised when using elevated total metal concentrations in stream sediments to infer anthropogenic contamination. A number of researchers have pointed to the importance of geological weathering and biological decomposition in causing the enrichment of metals within stream sediments (Sutherland 2000; Cal-Prieto et al. 2001; Munk and Faure 2004). El-Hasan and Jiries (2001) suggest that heavy metals generally occur in low concentrations in surficial environments. Consequently, elevated total metal values in stream and river sediments can be used to infer anthropogenic contamination (El-Hasan and Jires 2001). However, this is not necessarily the case because, even within a few meters in a local stream, changes in clay, carbon and sulfide content can significantly alter the scavenging capacity of these sediments for aqueous metals (Parker and Rae 1998; Munk and Faure 2004).

In this study, weathering of local bedrock is likely responsible for a substantial contribution to the metal values detected in the stream sediments. Furthermore, natural enrichment of Cd and Ni appears to be occurring within sediment in the headwaters of the Avondale Creek catchment system. Organic carbon concentrations here are extremely high (Figure 5-11). Thus, the Cd and Ni concentrations are likely controlled by the amount of C_{org} present in the stream sediment (Figure 5-11).

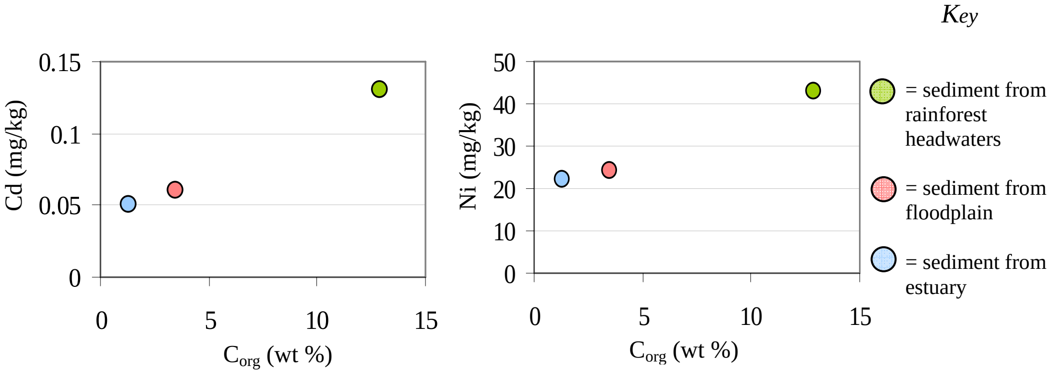

Figure 5-11: C_{org} values vs. Cd and Ni concentrations in stream and estuarine sediment from Avondale Creek. For each stream section, only one sample was analysed for C_{org} (S9, S21 and S25, respectively). Median values for Cd and Ni values in each section of the stream are given. For the sediment from the rainforest headwaters, n = 6; sediment taken from the floodplain section, n = 7; estuarine sediment, n = 2. Sample analyses were described in Chapter 2 – Section 2.4.7.1. Sample ID details are presented in Appendix A and data are shown in Appendix B.

Cadmium has been documented by Tada and Suzuki (1982) to possess a strong tendency to adsorb to organic matter in stream sediments. Furthermore, pronounced natural enrichment of Ni in organic-rich sediment from stream headwaters was reported by Sutherland et al. (2000). Sutherland et al.’s (2000) study location, a coastal rainforest stream system, was similar to that of this investigation. Hence, future studies examining sediment metal distributions in such environments need to be aware of the capacity of organic-rich materials present in these stream systems to accumulate metals.

Copper concentrations in the stream sediments collected from Avondale Creek remained relatively constant from the headwaters to the estuary mouth. Thus, there does not appear to be a Cu enrichment in this particular branch of the Avondale Creek catchment.

In contrast to the Cu result, Pb, Zn, Pd and Pt levels in the stream sediments increased downstream along the creek system. The maximum concentrations of these particular metals were present in the estuarine sediment samples (Table 5-2). In catchments that are not heavily impacted by anthropogenic processes, metal concentrations are commonly enriched in the sediment of the stream mouth and estuary. This is because these environments are conducive to the accumulation of organic matter, fine particles (namely clays) and sulfide minerals, all of which possess a strong scavenging capacity to adsorb suspended and dissolved metals from overlying waters (Parker and Rae 1998; Simpson et al. 2002; Caetano et al. 2003).

However, in this study the samples collected from the estuary mouth appeared to be atypical for estuary sediments. Visual inspection indicated they contained considerable amounts of coarse sand and their particle-size distribution showed a high level of silt-sized particles (Figure 5-2). The estuary mouth is situated among beach sand bars and appears to receive substantial input of sand washed and blown in from the coarse-grained littoral marine deposits; hence the presence of coarser sand particles in these mangrove estuary sediments. In fact, the particle-size distribution profile for the sediments collected from the floodplain section indicated a much greater abundance of fine material than for the estuary mouth (Figure 5-2).

Further to the above, the estuary sediment had a very low $S_{sulfide}$ content (Table 5-1) and contained relatively low levels of C_{org}, Fe_2O_3 and MnO (Table 5-1); materials which are renowned for sequestering metals. Estuarine sediments are acknowledged to have strong adsorptive properties (Tada and Suzuki 1982; Bordas and Bourg 2001; Cantwell et al. 2002). In contrast, sediment collected from the Avondale Creek estuary had a relatively low abundance of C_{org}, Fe_2O_3 and MnO (Table 5-1). Consequently, elevated Pb, Zn, Pd and Pt concentrations in the estuarine sediment collected in this study cannot be simply attributed to natural enrichment; instead, anthropogenic sources must be discussed.

5.4.3.2 Sewage discharge

Discharge from sewage treatment plants has been documented to introduce elevated metal loads to streams and estuaries (Lottermoser 1998; Cal-Prieto et al. 2001; Simonovski et al. 2003). The Smithfield Sewage Plant is situated adjacent to one of the tributaries of Avondale Creek. Anthropogenic metal concentrations detected in the stream and estuarine sediments analysed in this investigation were unlikely to be derived from discharge from this sewage plant, which is located on a different tributary of Avondale Creek to the one investigated in this study (Figure 5-1). During flooding, when overbank water from the various tributaries of the creek mix, some component of metal contamination from the sewage plant could conceivably enter other tributaries. However, because flooding events of this magnitude rarely occur, it is plausible to suggest that negligible amounts of metal contaminants in the tributary investigated in this study would be derived from the local sewage plant.

5.4.3.3 Fertilisers

Fertilisers have been documented as a source of heavy metals, particularly Cd, Cu and Zn, in contaminated stream bed sediments (Sutherland 2000). In this investigation, fertiliser represents a significant potential contributor to the elevated Zn levels detected in the estuarine sediment. Fertilisers rich in Zn are known to have been used on sugar crops in North Queensland (Grow Force Austalia Pty Ltd 2006). Some of these fertilisers, such as the Dissolvine Liquid Fertiliser, contain up to 50% Zn (Grow Force Austalia Pty Ltd 2006). Other fertilisers used in the sugar industry contain high levels (up to 100 mg/kg) of other metals, notably Cd which is associated with phosphorous (Incitec Pivot Limited 2006).

The major land use in the vicinity of this estuary is sugarcane plantations. Thus, the application of fertiliser on this crop may have led to the accumulation of Zn as well as other heavy metals. However, fertilisers are an unlikely source of metal contamination in the stream sediment samples collected upstream of the sugarcane crop.

5.4.3.4 Motor vehicles

So far it is suggested that natural processes accounted for the Cd, Cu and Ni concentrations in the stream sediment samples, while the use of fertiliser potentially caused the elevated Zn concentrations detected in the estuarine sediment. The increase in Pb and Pt concentrations in the stream sediment samples collected downstream of the Kuranda Range Road points towards road-related sources for these elevated metal levels.

Results from the Pb isotope analyses indicated contamination of anthropogenic Pb in the stream sediment collected downstream of the location where Avondale Creek is initially crossed by the Kuranda Range Road. Furthermore, total Pb concentrations increased from background levels in the first sample collected downstream from the road, while Pt concentrations gradually increased in the samples taken along the course of the catchment towards the estuary. Natural processes are unlikely to account for the selective enrichment of individual metals in the estuarine sediment. Moreover, the $S_{sulfide}$, C_{org}, Fe_2O_3 and MnO contents of the estuarine sediments were determined to be relatively low. These are all materials which have been documented to display strong affinities for adsorbing metals in streams (Parker and Rae 1998). Thus, urban runoff from road surfaces is concluded to be the likely primary source of the Pb and Pt content detected in the estuarine sediment. Both of these metals, particularly Pt, are distinctive tracers of motor-vehicle contamination (Sutherland 2000; Zereini and Alt 2000).

It should be noted that the concentration distribution profiles for Pb and Pt in the stream sediments differed from those documented for streams in other urban locations. For example, a study by dos-Reis et al. (2005), examining metal concentrations in stream and estuarine sediments in an industrial area in Portugal, showed that Pb values progressively decreased downstream of the industrial zone. The authors state that this distribution pattern for metals in fluvial and estuarine sedimentary deposits has been commonly documented; i.e. metal values are highest near the active pollutant source and gradually diminish downstream due to dilution (dos-Reis et al. 2005). In fact, the same conclusions were drawn in an investigation examining river bed sediment metal values in an industrialised region of Korea (Lee et al. 2003).

In contrast to the above, no point sources of metal were identified in this research. Thus, the insignificant dilution by other sediments originating in the floodplain and the constant input of metals from road surfaces into Avondale Creek likely explains the continual increase in stream sediment Pb and Pt values observed downstream along the course of the studied catchment. This finding may assist future studies examining Pb and Pt contamination within streams that are impacted by roads in non-industrialised locations. In such circumstances, it is recommended that metal values in sediments be measured over the total length of the stream rather than only within the stream section in the immediate vicinity of the road. This will provide a better understanding of the extent of the dispersion trail of these metal contaminants in non-industrialised areas.

This research has demonstrated that traffic-derived Pb and Pt are being dispersed to the fringe of the Great Barrier Reef by the Avondale Creek catchment system which receives runoff waters from nearby roads. There is the potential for these metal contaminants to be delivered to reef lagoonal systems by cyclonic events which can disperse stream sediments many kilometres offshore. Future studies may wish to explore the use of Pb isotopic ratios as they can be used for tracing contamination within offshore sediments (Munksgaard and Parry 2002).

5.4.4 Limitations in the use of Pb isotopes as tracers of traffic contamination

In Australia, where most Pb used in anthropogenic activities is of Proterozoic age, it is often difficult to distinguish between automotive-derived Pb and Pb produced from other anthropogenic sources, which include lead smelters, paints and pesticides (Gulson et al. 1981). While the use of Pb isotopes can distinguish anthropogenic from natural Pb in Australian soils and sediments, the isotopes cannot be conclusively used to appoint motor vehicles as the principal source of the Pb contamination.

For example, Lottermoser (1998) established Pb isotopic signatures in stream sediments in eastern Australia. A strongly non-radiogenic Pb signature was detected in those sediments collected from a heavily industrialised location, near the city of Newcastle. Whilst this signature could be reasonably inferred to represent anthropogenic Pb contamination in these sediments (again assuming that contaminant Pb in Australia is overwhelmingly derived from Proterozoic, non-radiogenic Pb deposits), the isotope ratios could not be used to discern specific sources of this contamination. Anthropogenic Pb in these sediments may have been a product of the accumulation of particulate Pb from automotive emissions, or from aerosol deposition of fine-particulate Pb from the long-running steel works in the area. Lead from both of these sources would exhibit strongly non-radiogenic isotopic signatures.

Therefore, most studies using Pb isotopes in Australia must rely on complementary evidence to Pb isotope ratios to apportion specific sources of Pb contamination. For example, Gulson et al. (1981) examined Pb isotopic ratios in rural topsoils in Australia. In their investigation, an assessment of the prevailing weather conditions, the distances of potential sources to the site, and the age of the Pb in the potential sources were used to infer long-range deposition of particulate Pb from petrol as the main source of this contamination (Gulson et al. 1981).

In a limited number of cases, distinct differences in the Pb isotope signatures of various anthropogenic Pb sources have been determined (Bing-Quan et al. 2001; DeVivo et al. 2001; Backstrom et al. 2004). Only in these studies have specific sources of Pb contamination been resolved based purely on Pb isotopic ratios.

In this study, the observed Pb contamination in the stream and estuarine sediments downstream of the Kuranda Range Road may be attributed to roadside sources. It was shown in Chapter 4 that road runoff waters, particularly ‘first flush’ waters, transport elevated metal concentrations. Moreover, there is a lack of any other anthropogenic Pb source within the proximity of the site. In this respect, this study is unique since the effects of automotive-derived Pb in the stream sediments analysed were able to be recognised without interference of other contributing Pb contaminant sources.

5.5 Conclusions

Geochemical analysis of stream and estuarine sediments from Avondale Creek revealed the dominance of anthropogenic sources for certain metals (Pb, Zn, Pd and Pt) and natural sources for others (Cd, Ni). The elevated Cd and Ni concentrations detected in stream sediments from the headwaters of the catchment system were attributed to natural enrichment by organic matter. In contrast, the elevated Pb, Zn and Pt contents in the stream and estuary sediments collected downstream of road crossings were credited to anthropogenic sources. This conclusion was supported by the anthropogenic Pb isotopic signatures detected in these sediments. Furthermore, the relatively low concentrations of adsorptive components (C_{org}, $S_{sulfide,}$ Fe_2O_3 and MnO) in the estuarine sediment precluded the likelihood of natural metal enrichment.

Zinc values rose sharply in the mangrove-supporting estuarine sediment of Avondale Creek, and this abrupt increase was attributed to an adjacent anthropogenic source, possibly fertiliser-laden runoff from adjoining sugarcane farms. Conversely, Pb sediment values showed a notable increase downstream of the first road crossing of Avondale Creek. Both Pb and Pt values steadily increased down the course of the stream into the estuary. Runoff waters from road surfaces were appointed as the major anthropogenic source of these metals in the stream and estuarine sediments; based on the lack of other likely repositories within the project area.

The downstream increase in sediment Pb and Pt values was credited to the diffuse ingress of road runoff waters into the stream, associated with insignificant dilution by other sediments originating in the floodplain. Consequently, future studies examining metal distribution in streams impacted by road drainage need to examine the entire stream length to achieve an understanding of the extent of the dispersion trail of metal contaminants in non-industrialised areas.

Finally, the research demonstrated that Pb and Pt derived from roadside sources in the wet-dry tropics in northern Australia have the potential to be transported into reef lagoonal systems during cyclonic and flooding events. Hence, research into metal contamination in reef lagoon sediments is recommended.

Chapter 6 Metal bioavailability in roadside soils and sediments

6.1 Introduction

It was demonstrated in Chapter 3 that traffic-derived metal contaminants are accumulating in road sediments on the Kuranda Range Road. It was also shown in Chapter 4 that a small proportion (<10 %) of these metals are readily mobilised in dissolved and suspended forms from the road's surface during rainfall events. The previous chapter (Chapter 5) showed that a distinctive signature of traffic-derived metal contamination was present, notably for Pb and Pt, in stream sediment samples collected downstream of the Kuranda Range Road. These findings warrant an assessment of the bioavailability of these traffic-derived metals.

An understanding of the bioavailability of metals which settle in roadside soil and sediment is essential to ascertain the degree to which these contaminants constitute an environmental risk. Only with the knowledge of the bioavailability of a given contaminant is it possible to establish: a) the need for some form of remediation to minimise the release of the contaminant into the environment; and b) options for remediation strategies, should any be required.

Two main methods are commonly used to assess the bioavailability of metals in the roadside environment as well as in other contaminated locations such as mining and industrial landscapes. These involve: a) the measurement of metal concentrations directly in the tissue and bones of organisms (e.g. Cook et al. 1994); and b) application of solutions designed to target the bioavailable fraction of metals in soil/sediment and the subsequent analysis of solutes (e.g. Onyatta and Huang 1998). The extraction solution method has the advantage over tissue analysis because it is often less expensive. However, results from studies that employ extraction solutions are simplistic since they can not take into account physiological differences between various species, or even different individuals of the same species. Despite this, extraction solution methods are generally seen as useful indicators of the bioavailable fraction of a given contaminant (Madrid et al. 2004).

Overall, studies which combine tissue and soil-extractable metal analyses provide the most comprehensive database regarding bioavailability.

The bioavailable portion of a given contaminant commonly comprises only a small fraction of its total presence in the environment. Nonetheless, studies into the presence of traffic-derived metals show that these contaminants are incorporated, to a varying degree, into animals, plants, fungi and bacteria that dwell in the immediate roadside environment.

Investigations by Weigmann (1991) and Marino et al. (1992) found elevated heavy metal levels in earthworms collected from sites in close proximities to major roads in Europe. Weigmann (1991) revealed that individuals of the earthworm species *Dendrobaena octaedra* living near highways hosted higher concentrations of Cd, Cu and Pb than those individuals dwelling at greater distances from roads. Also, the investigation by Marino et al. (1992) showed elevated Cu and Pb concentrations in five species of earthworm living immediately adjacent to the road. Moreover, research by Ward et al. (1975), David and Williams (1975), Wylie and Bell (1975), Wheeler and Rolfe (1979), Cook et al. (1994), Olajire and Ayodele (1997), Garcia and Millan (1998), Jaradat and Momani (1999) and Swaileh et al. (2004) has reported elevated concentrations of Cd, Cu, Pb, Ni and Zn in various species of bracken, grass and shrub growing in roadside topsoils.

In some instances, high levels of contaminants within plants are sourced from outside of the soil in which they grow. Airborne substances may settle directly onto vegetation. In such cases, a contaminant may be directly incorporated into a plant before it has the opportunity to settle in soil (Klumpp et al. 1999; Alaimo et al. 2000). Plants may derive considerable amounts of some elements through foliar absorption (Alloway 1995). Thus, some soil assessments may overlook the potentially important reservoir of bioavailable contaminants in airborne particulate matter. For example, studies by Garty et al. (1996) and Alaimo et al. (2000) determined that heavy metals associated with airborne particles are absorbed through the leaf and thalli surfaces of trees and lichen growing close to roads. Leaf and thalli tissue of the organisms analysed in their respective studies were found to host strongly elevated levels of Cd, Cu, Pb and Zn compared with the equivalent metal content of the soils in which they were growing (Garty et al. 1996; Alaimo et al. 2000).

The uptake of traffic-derived metal contaminants by organisms may have negative impacts on the health of roadside ecosystems (Burger et al. 2003; Hund-Rinke and Kordel 2003). Fish mortality downstream from roads has been related to excessive heavy metal (Cu and Zn) concentrations derived from roads (Forman and Alexander 1998). Moreover, metal contaminants may accumulate up the food-chain in the tissue of animals that feed on these roadside-dwelling organisms (Marino et al. 1992). Forman and Alexander (1998) reported elevated Pb levels in the tissue of mammals living in close proximity to roads.

Despite all of these previous studies, there are no data on the bioavailability of traffic-derived metals in roadside soils in wet-dry tropical regions. Thus, this chapter aims to establish the bioavailable portion of the heavy metals Cd, Cu, Pb, Ni and Zn in roadside soils and road sediments along the Kuranda Range Road. It is emphasised that this work does not examine the toxicity of these traffic metal contaminants. Such a study would require an assessment of intra-species parameters (e.g. age, gender), as well as concurrent analysis of several species (Burger et al. 2003). The objective of this research is to examine a single grass species to determine the extent to which traffic-derived heavy metals are bioavailable. The grass species *Melinis repens* (Red Natal grass) was used in this study as a marker of metal bioavailability.

6.2 Methods of analysis

Topsoil samples were taken adjacent to the Kuranda Range Road, 5 m from the road edge, and from a background field site (refer to Chapter 2 – Section 2.7.2 for methods and Appendix A for sample details). The topsoils were dried, sieved to less than 2 mm and analysed for their total Cd, Cu, Pb, Ni, Zn, Pd and Pt contents at ALS, Brisbane (Chapter 2 – Section 2.7.6).

Further to the above, extractions were performed on the topsoils using the DTPA bioavailable reagent (Chapter 2 – Section 2.7.4). The resulting extracts were analysed for their Cd, Cu, Pb, Ni and Zn values at the AAC, Townsville (Chapter 2 – Section 2.7.6).

Samples of the grass species *Melinis repens* were collected from the same locations as the topsoils (Appendix A). The grasses were washed, dried and separated into roots and stems (Chapter 2 – Section 2.7.2). Portions of the root and stem tissue of each sample were ashed and digested in HCl-H_2O_2 and analysed for their Cd, Cu, Pb, Ni and Zn contents (Chapter 2 – Sections 2.7.3, 2.7.6).

Finally, a greenhouse experiment was performed involving the planting of *M. repens* seeds in road sediments (Chapter 2 – Section 2.7.5). The substrates were watered daily and grasses were sampled upon maturity (i.e. when flowers developed). The greenhouse grasses were prepared in the same manner as the field *M. repens* grass samples (Chapter 2 – Section 2.7.3). Moreover, DTPA and EDTA-extractable metal values were determined in the road sediments used in the greenhouse experiment (Chapter 2 – Section 2.4.5.3).

6.3 Results

6.3.1 Topsoils

Topsoil samples (<10 cm bgs) collected from the immediate edge of the Kuranda Range Road, 5 m from the road edge and from a background site were analysed for their total Cd, Cu, Pb, Ni, Zn, Pd and Pt content (Table 6-1). Zinc was detected in higher concentrations than the other analytes in all soil samples (Table 6-1). The highest metal values were present in topsoil samples acquired from immediately next to the surfaced road edge and ranged from 0.008 – 0.016 mg Pd/kg to 144 – 1530 mg Zn/kg (Table 6-1). By comparison, the topsoils acquired 5 metres from the road edge hosted lower maximum, minimum and median topsoil Cd, Cu, Pb, Ni, Zn, Pd and Pt concentrations (Table 6-1). In contrast, the samples from the background site exhibited the lowest maximum, minimum and median Cu, Pb, Ni, Zn, Pd and Pt levels, ranging from 0.004 mg Pd and Pt/kg to 19 – 83 mg Zn/kg (Table 6-1). Maximum, minimum and median Cd values were higher in the background topsoil samples than in those samples collected 5 m from the road edge (Table 6-1).

A samples-paired T test was performed to establish whether road edge soil metal values were significantly higher than background levels. It was found that mean Cd, Pb, Ni and Zn values in the roadside topsoils were significantly higher ($p<0.05$) than their respective mean levels in the background soils.

Table 6-1: Total metal content of topsoil samples adjacent to the Kuranda Range Road, 5 m from the road edge and from a background site. All concentrations are reported in mg/kg. *For Pd and Pt, n = 2 for the road edge and 5 m locations, n = 1 for the background site. Refer to Chapter 2 – Section 2.7 for soil sampling details. Appendix A presents topsoil sample ID descriptions and the data for individual topsoil samples are given in Appendix B.

	Road edge (n = 7)		5 m from road edge (n = 4)		Background (n = 5)	
	Range	*Median*	*Range*	*Median*	*Range*	*Median*
Cd	0.08 – 0.49	0.2	0.01 – 0.06	0.05	0.05 – 0.12	0.09
Cu	33 – 250	61.1	16.7 – 54	31.4	3.1 – 7.3	5.8
Pb	35.6 – 185	97.3	14.6 – 43.7	19.2	10 – 13.2	11.2
Ni	14.6 – 44	28.6	7.2 – 28.2	18.9	3 – 5.7	3.7
Zn	144 – 1530	729	54 – 146	129	19 – 83	21
Pd*	0.008 – 0.016	-	0.004 – 0.006	-	0.004	-
Pt*	0.0128 – 0.0319	-	0.0049 – 0.0058	-	0.004	-

6.3.2 Grass specimens

Specimens of the grass species *Melinis repens* (*M. repens*) were collected from the same locations as the topsoil samples (i.e. from the immediate edge of the Kuranda Range Road, 5 m from the road edge and from a background site). The root and stem tissue of each sample were separated from each other and analysed for their total heavy metal (Cd, Cu, Pb, Ni and Zn) contents. Table 6-2 presents the concentration data for the grass samples and all values are reported relative to the dry weight of the samples.

Zinc was detected in higher concentrations than the other metals in all stem and root samples (Table 6-2). Maximum and minimum metal values in the grasses varied between the different locations. In the stems, the highest median Cu, Ni and Zn concentrations were present in the *M. repens* specimens collected adjacent to the road edge, reaching up to 232 mg Zn/kg (Table 6-2). In contrast, the highest median Cd (0.078 mg/kg) and Pb (1.79 mg/kg) levels were detected in the stems of the *M. repens* samples acquired from the background site (Table 6-2).

In the root tissue, the *M. repens* specimens collected immediately adjacent to the Kuranda Range Road edge exhibited the highest median Cu, Pb, Ni and Zn concentrations, ranging up to 169 mg Zn/kg (Table 6-2). At a distance of approximately 5 m away from the road edge, much lower Cu, Pb, Ni and Zn concentrations were observed in the root tissue of the *M. repens* samples (Table 6-2). The root tissue of the grass samples collected from the background site displayed the lowest median Cu, Pb, Ni and Zn values (Table 6-2).

In contrast to the distribution of the other metals in the roots of the studied grasses, the highest median Cd concentration was recorded in the *M. repens* specimens taken from the background site (Table 6-2). Furthermore, the root samples collected 5 m from the road edge yielded the lowest median Cd value (Table 6-2).

A statistically significant ($p<0.05$) difference was observed between the mean Zn value in the roadside stems compared with the background stems. Moreover, for the roots, mean Cu, Ni and Zn values were significantly ($p<0.05$) higher in the road edge samples in relation to the background specimens.

Table 6-2: Total metal content of *M. repens* samples collected from the project area. Concentrations in mg/kg are reported relative to the dry weight of each sample. Refer to Chapter 2 – Section 2.7 for grass sampling details. Appendix A presents grass sample ID descriptions and the data for individual grass samples are given in Appendix B.

	Stem tissue					
	Road edge (n = 7)		5 m from road edge (n = 4)		Background (n = 5)	
	Range	*Median*	*Range*	*Median*	*Range*	*Median*
Cd	0.027 – 0.062	0.050	0.028 – 0.043	0.038	0.028 – 0.257	0.078
Cu	1.85 – 3.74	3.16	1.71 – 3.74	2.06	1.90 – 8.90	2.62
Pb	0.57 – 14	1.06	0.70 – 2.26	0.82	1.02 – 11.1	1.79
Ni	0.51 – 1.60	0.73	0.24 – 0.67	0.38	0.17 – 0.50	0.35
Zn	101 – 326	231.6	35.6 – 73.3	64.9	18.1 – 50.1	40.8
	Root tissue					
	Road edge (n = 7)		5 m from road edge (n = 4)		Background (n = 5)	
	Range	*Median*	*Range*	*Median*	*Range*	*Median*
Cd	0.118 – 0.223	0.128	0.064 – 0.172	0.091	0.131 – 0.658	0.183
Cu	15.7 – 41.3	29.1	9.33 – 24.5	14.8	4.58 – 19.6	5.98
Pb	5.24 – 17.9	7.82	2.81 – 9.65	4.53	2.09 – 18.5	4.03
Ni	1.65 – 5.80	2.73	1.21 – 6.51	1.75	0.58 – 2.60	0.70
Zn	38.8 – 362	169	21.2 – 52.1	30.1	11.5 – 22.6	22

Ratios between stem and root tissue metal values in the *M. repens* samples were calculated and are plotted in Table 6-3. Cadmium, Cu, Pb and Ni concentrations were consistently higher in the root tissue than the stems of the *M. repens* specimens analysed in this study (Table 6-3). Moreover, ratios between root and stem Cd, Cu, Pb and Ni levels were greatest for the samples collected immediately adjacent to the road edge (Table 6-3). The ratios were slightly lower, with the exception of Ni, in the samples taken 5 m from the road (Table 6-3). In comparison, the *M. repens* specimens acquired from the background field exhibited the lowest root versus stem Cd, Cu, Pb and Ni ratios (Table 6-3). Zinc displayed a contrasting distribution pattern to the other metals in the studied *M. repens* samples (Table 6-3). Specifically, Zn values were higher in the stems than in the roots for all analysed grass specimens (Table 6-3). The root versus stem Zn ratio was greatest for the *M. repens* samples collected immediately adjacent to the road edge (Table 6-3).

Table 6-3: Root/stem metal value ratios in *M. repens* samples. Median values were used to calculate ratios.

	Road edge (n = 7)	5 m from road edge (n = 4)	Background (n = 5)
Cd	2.6	2.4	2.3
Cu	9.2	7.2	2.3
Pb	7.4	5.5	2.3
Ni	3.7	4.6	2
Zn	0.7	0.5	0.5

6.3.3 DTPA extractions

DTPA-extractable metal values were determined for the topsoil samples collected from the project area and the data are presented in Table 6-4. The extractions were performed adhering to the procedure stipulated by Rayment and Higginson (1992) (Appendix C).

Soil-DTPA metal values exhibited similar patterns to total soil metal concentrations (Table 6-4). Maximum and minimum soil-DTPA metal values were highest in the samples collected immediately adjacent to the Kuranda Range Road edge, ranging from 0.02 – 0.18 mg Cd/kg to 15 – 588 mg Zn/kg (Table 6-4). Median soil-DTPA values were also highest for all metals in the road edge topsoils, ranging from 0.04 mg Cd/kg to 263 mg Zn/kg (Table 6-4). Maximum, minimum and median soil-DTPA concentrations were distinctly lower in the samples taken 5 m away from the road (Table 6-4). By comparison, the topsoil samples acquired from the background site yielded the lowest soil-DTPA metal values (Table 6-4). Mean Cu and Zn values were significantly ($p<0.05$) higher in the road edge samples in relation to the background specimens.

Table 6-4: DTPA-extractable metal concentrations from topsoils collected: immediately adjacent to the Kuranda Range Road edge; 5 m from the road edge; and from a background site. The solid concentrations are expressed in mg/kg. Refer to Chapter 2 – Section 2.7 for soil extraction details. Appendix A presents extract sample ID descriptions and the data for extract samples are given in Appendix B. Note the liquid extract values in Appendix B have been multiplied by a factor of 2 to obtain the solid dry weight values because a 2:1 liquid/solid ratio was used in the extractions.

	Road edge (n = 7)		5 m from road edge (n = 4)		Background (n = 5)	
	Range	*Median*	*Range*	*Median*	*Range*	*Median*
Cd	0.02 – 0.18	0.04	0.02 – 0.02	0.02	0.02 – 0.06	0.02
Cu	2.1 – 9.36	6.00	0.62 – 4.68	1.94	0.1 – 5.4	0.16
Pb	8.8 – 45.4	17.3	1.02 – 12.42	2.44	1.64 – 3.16	2.72
Ni	0.08 – 2.06	0.84	0.02 – 0.46	0.28	0.02 – 0.28	0.02
Zn	15 – 588	263	12.6 – 43.6	13	1.2 – 4.4	1.82

The proportion of each metal extracted by the DTPA solution was calculated relative to its total content in the topsoil samples. The bioavailable metal proportion in individual topsoil samples was calculated by dividing the DTPA-extractable soil concentration (in dry weight mg/kg) by the total soil metal value (mg/kg). The resulting values were then converted to percentages. Median bioavailable proportion values for the analysed metals are shown in Table 6-5.

The results demonstrated that Cd was extracted from the topsoils by the DTPA reagent in greater proportion than any of the other studied metals (Table 6-5). In contrast, Ni showed the lowest bioavailable fraction in the topsoils (Table 6-5). The bioavailable proportions of Cu, Ni and Zn were highest in the road edge samples and decreased in the topsoils taken 5 m from the road edge (Table 6-5). By comparison, the background topsoil samples exhibited the lowest bioavailable Cu, Ni and Zn fractions (Table 6-5). The bioavailable proportions of Cd and Pb, however, were highest in the topsoil samples acquired 5 m from the road edge and from the background site, respectively (Table 6-5).

Table 6-5: Proportions of DTPA-extractable metal values relative to total metal contents in topsoil samples from: the edge of the Kuranda Range Road (n = 7); 5 m from the road edge (n = 4); and from the background site (n = 5). The results are expressed as percentages of the total individual metal contents. Median values are shown.

	Bioavailable proportions (%)				
	Cd	**Cu**	**Pb**	**Ni**	**Zn**
Road edge	25	9	21	2.2	30
5 m from road edge	40	6.5	12.5	1.6	10.5
Background site	29	4	24	0.6	6

6.3.4 Greenhouse experiment

6.3.4.1 Grass specimens

The bioavailability of heavy metals in road sediments was assessed by a greenhouse trial involving the grass species *M. repens*. Two pots were used in the experiment: the first pot contained sediments from the Kuranda Range Road, the other had road sediments from the Captain Cook Highway roundabouts. Two grass samples grown in Kuranda Range Road sediments and one sample from the Captain Cook Highway roundabout sediments were collected. The stem and root tissue of the specimens was analysed for their total Cd, Cu, Pb, Ni and Zn contents and the data are shown in Table 6-6.

Metal values were similar for grass specimens from both pots (Table 6-6). Zinc was detected in higher concentrations than the other metals in all *M. repens* samples grown in the greenhouse pots (Table 6-6). The maximum Zn concentration of 1246 mg/kg was recorded in the stem tissue of one of the samples grown in the Kuranda Range Road sediments (Table 6-6). In contrast, Cd was detected in lower concentrations than the other metals in the greenhouse grass samples (Table 6-6).

The root tissue of the greenhouse grasses hosted higher Cd, Cu, Pb and Ni concentrations than the stem tissue (Table 6-6). However, stem tissue Zn values were lower than root tissue Zn levels for all greenhouse *M. repens* samples (Table 6-6).

Table 6-6: Metal concentrations (mg/kg) in *M. repens* samples grown in the greenhouse experiment. Concentrations are reported relative to the dry weights of the samples. Refer to Chapter 2 – Section 2.7 for greenhouse experiment details. Appendix A presents greenhouse sample ID descriptions and the data for individual samples are given in Appendix B.

	Grasses grown in Kuranda Range Road sediments (n = 2)		Grasses grown in Captain Cook Highway roundabout sediments (n = 1)
	Stem tissue		
	Range	***Mean***	
Cd	0.025 – 0.075	0.05	0.16
Cu	3.9 – 6.3	5.1	5.2
Pb	2.4 – 3.4	2.9	0.45
Ni	1.0 – 1.2	1.1	1.24
Zn	552 – 1250	899	1210
	Root tissue		
	Range	***Mean***	
Cd	0.08 – 0.18	0.13	0.2
Cu	86 – 122	104	54
Pb	2.1 – 2.9	2.5	6.7
Ni	3.3 – 6.3	4.8	2.1
Zn	105 – 225	165	254

6.3.4.2 Metal extractability in the road sediments

The correlation between DTPA and Ethylenediaminetetraacetic (EDTA) - extractable heavy metal concentrations in the road sediments was investigated in order to compare the results yielded by the two extraction reagents. The correlation analysis was performed on log-normalised data and the results in Figure 6-1 show that DTPA and EDTA-extractable metal values are positively correlated ($R^2 = 0.96$). Moreover, the correlation is significant at the $p<0.01$ level. The EDTA extraction solution liberated greater amounts of metal from the sediment samples than did the DTPA solution. The average ratio between EDTA-extracted metal values and DTPA-extracted concentrations is 1.6/1.

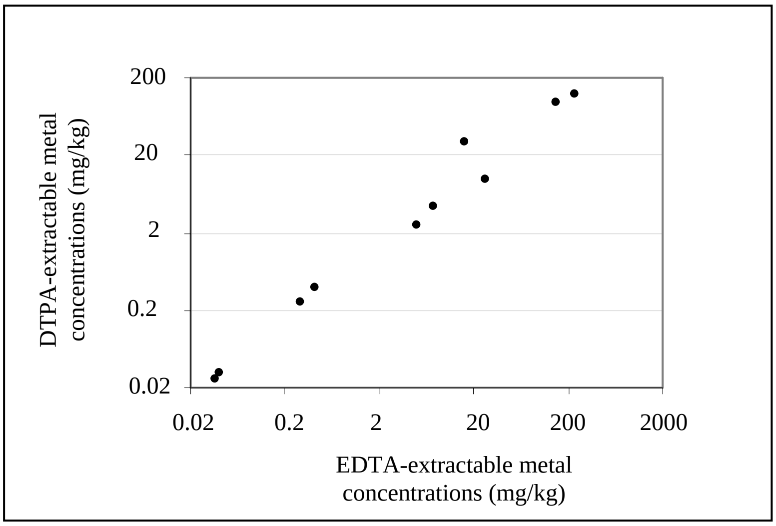

Figure 6-1: DTPA-extractable vs. EDTA-extractable metal concentrations in road sediments from the Kuranda Range Road and the Captain Cook Highway roundabouts. n = 10. Refer to Chapter 2 – Section 2.4.5.3 for sediment bioavailable extraction procedures. Appendix A presents sample ID descriptions for the extracts and the data for individual samples are given in Appendix B.

The bioavailable proportions of the studied metals in the road sediments were calculated from results of the DTPA and EDTA extractions and the values are presented in Table 6-7. Soil-extractable values were converted from aqueous to solid concentrations (by multiplying the aqueous values by a factor of 2 considering a liquid/solid ratio of 2:1). The results reveal that bioavailable metal proportions in the road sediments were lower than in the roadside topsoils (Table 6-5). Zinc displayed the highest and Ni the lowest bioavailable proportions in the Kuranda Range Road sediments (Table 6-7). In contrast, Pb exhibited the highest bioavailable fraction in the Captain Cook Highway roundabout sediments (Table 6-7).

Table 6-7: Proportions of DTPA and EDTA-extractable metal values relative to total metal contents in road sediment samples from the Kuranda Range Road (n = 4) and the Captain Cook Highway roundabouts (n = 4). The results are expressed as percentages of the total individual metal contents. Mean values are shown.

		Bioavailable proportions (%)				
Sediment source		**Cd**	**Cu**	**Pb**	**Ni**	**Zn**
Kuranda Range Road	DTPA-extractable proportions	7	4.5	6.5	1.0	9
	EDTA-extractable proportions	10.4	9.4	11.7	1.1	18
Captain Cook Highway roundabouts	DTPA-extractable proportions	10.8	9	27	0.6	13
	EDTA-extractable proportions	14.1	25	15	0.7	22

6.4 Discussion

6.4.1 Heavy metal and PGE contamination of roadside topsoils

Soils represent an important repository for metals. Soil-hosted metals may become remobilised upon interaction with water or be dispersed into freshwater systems by wind, water or gravity (Trombulak and Frissell 2000).

Results shown in Table 6-1 clearly demonstrated the contamination of topsoils adjacent to the Kuranda Range Road by heavy metals and PGEs. The differences in total Cd, Cu, Pb, Ni and Zn concentrations between the road edge samples and those collected at a distance of approximately 5 metres from the road edge are particularly distinct. Median Pb, Zn, Pt and Pd concentrations in the road edge topsoil samples were strongly elevated relative to their respective values in the soil samples collected at a distance of 5 metres from the road edge. Consequently, it is likely that motor vehicles and road infrastructure, such as signposts and road paving materials, represent the predominant sources of these contaminants in the soils at the edge of the Kuranda Range Road.

The observed decrease of soil-metal concentrations at a distance of only 5 m from the road edge in this study is in good agreement with other investigations that have assessed topsoil metal contamination adjacent to roads. For example, Clift et al. (1983) investigated soil contamination adjacent to a major highway in Victoria, and these authors detected that topsoil Pb concentrations decreased sharply at a distance of approximately 5 metres from the road edge. Similarly, an examination of soil Pb adjacent to a major road in Perth, showed that topsoil Pb levels diminished dramatically at distances of approximately 5 to 10 m from the road edge (Bottomley and Boujos 1975). Furthermore, Dierkes and Geiger (1999) found that the Cd, Cu, Pb and Zn concentrations in topsoils decreased considerably at distances of 5 m away from the edge of the A2 Highway in Gelsenkirchen, Germany.

The total soil-metal values recorded adjacent to the Kuranda Range Road by this study are commensurate with those detected in various roadside soils by other investigations (Table 6-8). Yet, the Pb concentrations in the topsoils studied herein were much higher than those documented for soils adjacent to a road in France with a similar traffic volume to the Kuranda Range Road (Piron-Frenet et al. 1994). In addition, the median Zn concentration found in the topsoils collected adjacent to the Kuranda Range Road exceeded Zn topsoil values reported in soils adjacent to much more heavily trafficked roads (Table 6-8). Moreover, the metal levels in the studied topsoil specimens are similar to soil metal values (Cu = 44 mg/kg, Pb = 203 mg/kg, Zn = 224 mg/kg) recorded in the inner Sydney area (Snowdon and Birch 2004). Snowden and Birch (2004) report that over the past 150 years, soils in inner Sydney have been impacted by coal and chemical works, brass foundries, port operations, tanneries and refineries. The fact that the roadside soil metal values in this study are comparable to, and for Zn elevated above, those levels documented by Snowden and Birch (2004), attests to the high level of contamination that can build-up in roadside corridors. Causes for this build-up of Zn in the Kuranda Range Road topsoils may be related to the high abrasion rates of tyres on the road surface, as was discussed in Chapter 3.

Clearly, the topsoils immediately adjacent to the Kuranda Range Road are effective sinks for traffic-derived metals, most notably Zn. It is therefore important to investigate the bioavailable portion of these soil-hosted metals, as little is known regarding the lability of these contaminants in roadside corridors within wet-dry tropical locations (Turner and Maynard 2003).

Table 6-8: Heavy metal and PGE concentrations in roadside topsoils throughout the world.

	Mean concentration in road edge soil (mg/kg)	***Location***	***Author***
Cd	3.9	A2 Highway, Gelsenkirchen, Germany, 107 600 ADT	Dierkes and Geiger (1999)
	0.76	Busy road, Osogbo, Nigeria	Fakayode and Olu-Owolabi (2003)
	(Range) 0.01 – 0.12	Major roads, Lagos, Nigeria	Awofolu (2005)
	(median value) 0.2	Kuranda Range Road, 6 126 ADT	This study
Cu	413	A2 Highway, Gelsenkirchen, Germany, 107 600 ADT	Dierkes and Geiger (1999)
	180	Corpus Christi, Texas, USA, 48 000 ADT	Turner and Maynard (2003)
	28	Busy road, Osogbo, Nigeria	Fakayode and Olu-Owolabi (2003)
	(Range) 0.1 – 2.90	Major roads, Lagos, Nigeria	Awofolu (2005)
	(median value) 61.1	Kuranda Range Road, 6 126 ADT	This study
Pb	239	A2 Highway, Gelsenkirchen, Germany, 107 600 ADT	Dierkes and Geiger (1999)
	730	Corpus Christi, Texas, USA, 48 000 ADT	Turner and Maynard (2003)
	1200	Mulgrave Freeway, Victoria, Aust., 40 000 ADT	Clift et al. (1983)
	8	Minor Road, Beauvoir-sur-Mer, France, 5 250 ADT	Piron-Frenet et al. (1994)
	195	Minor Road, Beauvoir-sur-Mer, France, 19 049 ADT	Piron-Frenet et al. (1994)
	92	Busy road, Osogbo, Nigeria	Fakayode and Olu-Owolabi (2003)
	(Range) 0.02 – 0.23	Major roads, Lagos, Nigeria	Awofolu (2005)
	(median value) 97.3	Kuranda Range Road, 6 126 ADT	This study
Ni	46	Corpus Christi, Texas, USA, 48 000 ADT	Turner and Maynard (2003)
	9.65	Busy road, Osogbo, Nigeria	Fakayode and Olu-Owolabi (2003)
	(median value) 28.6	Kuranda Range Road, 6 126 ADT	This study
Zn	527	A2 Highway, Gelsenkirchen, Germany, 107 600 ADT	Dierkes and Geiger (1999)
	390	Corpus Christi, Texas, USA, 48 000 ADT	Turner and Maynard (2003)
	56.27	Busy road, Osogbo, Nigeria	Fakayode and Olu-Owolabi (2003)
	(Range) 0.51 – 3.35	Major roads, Lagos, Nigeria	Awofolu (2005)
	(median value) 729	Kuranda Range Road, 6 126 ADT	This study
Pd	0.011	Stuttgart, Germany, 120 000 ADT	(Schafer and Puchelt 1998)
	(median value) 0.012	Kuranda Range Road, 6126 ADT	This study
Pt	0.180	Stuttgart, Germany, 120 000 ADT	(Schafer and Puchelt 1998)
	(median value) 0.0224	Kuranda Range Road, 6126 ADT	This study

6.4.2 Metal levels in stem tissue of *M. repens*

Metal concentrations in the *M. repens* samples collected adjacent to the edge of the Kuranda Range Road provide a direct measure of the bioavailability of soil-hosted metals. The stem tissue of the *M. repens* specimens taken next to the road edge exhibited low Cd, Cu, Pb and Ni values relative to their respective concentrations in the samples acquired from the background site (Table 6-2). Thus, it is concluded that these particular metals are not accumulating in the above-ground tissue of those grasses growing immediately adjacent to the road edge, despite the high metal levels occurring in the roadside substrates.

Stem Zn concentrations, however, were considerably elevated in the roadside specimens of *M. repens* compared with the background samples (Table 6-2). This is strong evidence that the high Zn levels detected in the roadside topsoils are readily bioavailable to the above-ground tissue of the *M. repens* specimens growing next to the Kuranda Range Road.

No studies have investigated heavy metal uptake by the species *M. repens*. Consequently, the findings of this investigation can only be discussed in comparison with other vegetation species examined in the literature. Roadside grass and plant concentration data from this research and other studies are pooled in Table 6-9.

The median Cd concentration of 0.05 mg/kg for the roadside *M. repens* stems is within the reported range of Cd levels (0.01 mg/kg to 0.18 mg/kg dry weight) in other plant stems from roadside environments (Table 6-9). Also, Cd has been detected in concentrations below 1 mg/kg in the above ground tissue of roadside bracken (*Pteridium esculentum),* grasses (*Lolium sp*., unspecified) and flowering shrubs (*Inula viscose)* (David and Williams 1975; Olajire and Ayodele 1997; Garcia and Millan 1998; Swaileh et al. 2004; Awofolu 2005). Results from previous work suggest that the Cd concentrations in roadside topsoils are commonly two to five times higher than the Cd concentrations in the stems of roadside vegetation (Table 6-11).

In comparison to Cd, stem Cu concentrations in the *M. repens* specimens, with a median value of 3.2 mg/kg for the road edge samples, were much lower in this investigation than in other studies (Table 6-9). The stem Cu contents of roadside shrubs (*Taraxacum spp., Anabasis Articulata),* flowering plants *(Inula viscose*), bracken (*Pteridium esculentum)* and grasses (*Lolium sp*.) have been reported to be between 4 mg/kg and 60 mg/kg (David and Williams 1975; Cook et al. 1994; Olajire and Ayodele 1997; Garcia and Millan 1998; Jaradat and Momani 1999; Swaileh et al. 2004). In contrast, grass tissue Cu levels were lower in the investigation by Awofolu (2005) than those reported in this study. Furthermore, previous studies have reported poor associations between topsoil Cu values and the levels of this metal in the stems of roadside plant species (David and Williams

1975; Cook et al. 1994; Olajire and Ayodele 1997; Jaradat and Momani 1999; Swaileh et al. 2004; Awofolu 2005).

The roadside *M. repens* stems examined in this research displayed relatively low Pb values compared with concentrations recorded in the above-ground tissue of other roadside plants and grasses (Table 6-9). Previous studies have demonstrated that Pb concentrations are highly variable in the stem tissue of shrubs and grasses growing next to road edges. For example, Garcia and Millan (1998) studied the uptake of heavy metals in roadside grasses (*Lolium sp.*) in Spain. In this species, the stem Pb levels were very low; consistently below 10 mg/kg. Soil Pb levels in which the roadside grasses were growing were considerably higher, reaching values of 700 mg/kg. In contrast, Ward et al. (1975) determined Pb concentrations of 700 mg/kg in the stem tissue of cottonwood shrub specimens growing next to a remote highway in the North Island of New Zealand. These Pb levels were very high, considering that the ADT of the highway was only 1200 and the topsoil Pb levels adjacent to the road were only 160 mg/kg. Commonly, Pb concentrations in roadside plant tissue are much lower than the respective Pb levels in the topsoil which hosts the plants (Garcia and Millan 1998; Jaradat and Momani 1999) (Table 6-11). Similarly, this study revealed that Pb values in the *M. repens* stems were much lower than soil Pb values adjacent to the edge of the Kuranda Range Road.

There is very little published data on Ni contamination in roadside plant species. However, Ni levels in the stems of the *M. repens* samples collected from the edge of the Kuranda Range Road were much lower than the Ni values documented in the stems of other roadside plants and grasses. For example, Swaileh et al. (2004) found higher Ni levels (4.9 mg/kg) in the stems of *Inula viscose*, a small flowering plant growing adjacent to a major highway in the West Bank. This was despite the lower Ni roadside topsoil levels encountered in their investigation (18.7 mg/kg) compared with this study (28.6 mg/kg). In contrast, work by Olajire and Ayodele (1997) revealed a relatively high Ni topsoil concentration of 115 mg/kg next to a major road in Nigeria. However, a comparatively low Ni level (10.9 mg/kg) was recorded in the stems of an unspecified grass species growing at the roadside (Olajire and Ayodele 1997).

The Zn concentration recorded in the *M. repens* stems in this study (median value of 231 mg/kg) was much greater than the Zn stem tissue levels of roadside grasses (*Lolium sp.*, unspecified), woody shrubs (*Taraxacum spp., Anabasis*

Articulata), small flowering plants (*Inula viscose*) and bracken (*Pteridium esculentum*) recorded in the literature. Studies by David and Williams (1975), Cook et al. (1994), Olajire and Ayodele (1997), Jaradat and Momani (1999), Garcia and Millan (1998), Swaileh et al. (2004) and Awofolu (2005) all report Zn concentrations of between 0.19 mg/kg and 130 mg/kg for the stem tissue of the above-listed species.

The high topsoil Zn concentrations documented adjacent to the Kuranda Range Road have led to high Zn values in the stem tissue of *M. repens* specimens growing in these soils. It is obvious that this metal is strongly available to vegetation growing adjacent to roads. Zinc in roadside topsoils has been documented to be readily taken-up by the above-ground tissue of roadside plants (David and Williams 1975; Jaradat and Momani 1999).

6.4.3 Metal levels in root tissue of *M. repens*

Root tissue metal concentrations were generally higher than stem tissue metal concentrations in the *M. repens* samples analysed in this study. Moreover, the root tissue of the roadside grasses clearly exhibited higher metal levels than the roots of specimens taken away from the road. These results indicate that elevated topsoil levels of these metals next to the Kuranda Range Road have led to their uptake by the root system of the *M. repens* specimens growing in the roadside deposits.

Copper and Zn exhibited the highest values in the root tissue of the roadside *M. repens* samples. This result is expected given that of the metals analysed, only Cu and Zn are essential elements for plants (Siegel 2002). The median concentrations of Cu and Zn in the root tissue of the road edge *M. repens* specimens were 29.1 mg/kg and 169 mg/kg, respectively. These values are elevated above the “average chemical composition” values for “plants” which are 9 mg/kg for Cu and 70 mg/kg for Zn, according to Faure (1991).

To date, there has been only one study documenting metal levels within the root tissue of roadside plants. Cook et al. (1994) examined metal uptake by the stem and root tissue of a woody shrub (*Taraxacum spp.*) adjacent to a highway in Greece. Their results indicate a greater range of Cu and Pb levels in the root tissue of the roadside plants when compared with the stems, with higher levels of these metals generally present in the roots. Zinc concentrations, however, were found to be higher in the stem tissue of the shrub specimens (Cook et al. 1994). Thus, their findings are in good agreement with those of this research despite differences in the vegetation type, examined, shrub rather than grass.

Table 6-9: Metal concentrations in the stem tissue of various roadside plants. Values are presented relative to dry weight for each species. *P* = plant, *S* = soil. * denotes that portion of plant analysed has not been specified.

Author/plant species	**Road studied/traffic density (where given)**	**Metal concentrations (mg/kg)**									
		Cd		*Cu*		*Pb*		*Ni*		*Zn*	
		P	*S*	*P*	*S*	*P*	*S*	*P*	*S*	*P*	*S*
This study/*Melinis repens*	Kuranda Range Road/ 6 126 ADT	0.05	0.2	3.2	61.1	1.1	97.3	0.7	28.6	232	729
Cook et al. (1994) / *Taraxacum spp.*	Highway, Thessaloniki, Greece	-	-	57	210	85	620	-	-	130	590
David and Williams (1975)/ *Pteridium esculentum* (bracken)	Hume Highway, NSW, Australia	0.04	0.06	4.7	1.5	19.1	12.4	-	-	52	29
Jaradat and Momani (1999)/ *Anabasis Articulata* (woody shrub)	Highway, Amman, Jordan	-	-	31.3	29.7	7.3	189	-	-	99	122
Ward et al. (1975)/ *Cassinia vauvilliersii* (Cottonwood)	State Highway, New Zealand/ 1 200 ADT	-	-	-	-	700	160	-	-	-	-
Wylie and Bell (1973)/ *Chloris gayana* (grass)	Cunningham Highway, South East Queensland, Australia/ 16 000 ADT	-	-	-	-	41 and 64	84 and 207	-	-	-	-
*Garcia and Millan (1998)/ *Lolium sp.* (grass)	Main Road, Gipuzkoa, Spain/ 30 700 ADT	0.13	0.84	10.8	162	5.1	471	-	-	27	463
Swaileh et al. (2004)/ *Inula viscose* (small flowering plant)	Nablus-Ramallah Hwy, West Bank/ 120 000 ADT	0.10	0.27	10.6	60.4	7.3	87.4	4.9	18.9	48	82
Olajire and Ayodele (1997)/ grass sp.	Ibadan, Nigeria	0.18	2.7	8.9	80.5	205	730	10.9	115	43.5	213
Wheeler and Rolfe (1979)/ *Poa pratensis* (bluegrass*)*	Highway, Illinois, USA/ 8 100 ADT	-	-	-	-	195	1220	-	-	-	-
*Awofolu (2005)/common grass	Major roads, Lagos, Nigeria/ 10 000 ADT approx.	0.01 to 0.07	0.01 to 0.12	0.1 to 1.48	0.1 to 2.90	0.01 to 0.14	0.02 to 0.23	-	-	0.19 to 1.80	0.51 to 3.35

Table 6-10: Metal concentrations in the root tissue of various roadside plants. Values are presented relative to dry weight for each species. *P* = plant, *S* = soil.

Author/plant species	Road studied/traffic density (where given)	Metal concentrations (mg/kg)									
		Cd		*Cu*		*Pb*		*Ni*		*Zn*	
		P	*S*	*P*	*S*	*P*	*S*	*P*	*S*	*P*	*S*
This study/*Melinis repens*	Kuranda Range Road/ 6 126 ADT	0.13	0.2	29.1	61.1	7.8	97.3	2.7	28.6	169	729
Cook et al. (1994) / *Taraxacum spp.*	Highway, Thessaloniki, Greece	-	-	71	210	114	620	-	-	102	590

Table 6-11: Soil/plant metal concentration ratios (stem tissue). * denotes that portion of plant analysed has not been specified.

Author/plant species	Road studied/traffic density (where given)	Soil concentration/plant dry weight concentration				
		Cd	*Cu*	*Pb*	*Ni*	*Zn*
This study/*Melinis repens*	Kuranda Range Road/ 6 126 ADT	4	19.4	91.7	39.1	3.1
Cook et al. (1994) / *Taraxacum spp.*	Highway, Thessaloniki, Greece	-	3.7	7.3	-	4.5
David and Williams (1975)/ *Pteridium esculentum* (bracken)	Hume Highway, NSW, Australia	1.6	0.3	0.6	-	0.6
Jaradat and Momani (1999)/ *Anabasis Articulata* (woody shrub)	Highway, Amman, Jordan	-	0.9	25.9	-	1.2
Ward et al. (1975)/ *Cassinia vauvilliersii* (Cottonwood)	State Highway, New Zealand/ 1 200 ADT	-	-	0.20	-	-
Wylie and Bell (1973)/ *Chloris gayana* (grass)	Cunningham Highway, South East Queensland, Australia/ 16 000 ADT	-	-	2 to 3.5	-	-
*Garcia and Millan (1998)/ *Lolium sp.* (grass)	Main Road, Gipuzkoa, Spain/ 30 700 ADT	6.5	15	92.4	-	17.2
Swaileh et al. (2004)/ *Inula viscose* (small flowering plant)	Nablus-Ramallah Hwy, West Bank/ 120 000 ADT	2.7	5.7	12.1	3.9	1.7
Olajire and Ayodele (1997)/ grass sp.	Ibadan, Nigeria	15	9	3.6	11	4.9
Wheeler and Rolfe (1979)/ *Poa pratensis* (bluegrass)	Highway, Illinois, USA/ 8 100 ADT	-	-	6.3	-	-
*Awofolu (2005)/common grass	Major roads, Lagos, Nigeria/ 10 000 ADT approx.	1 to 1.7	1 to 2.0	1.6 to 2.0	-	1.9 to 2.7

Table 6-12: Soil/plant metal concentration ratios (root tissue).

Author/plant species	**Road studied/traffic density (where given)**	**Soil concentration/plant dry weight concentration**				
		Cd	*Cu*	*Pb*	*Ni*	*Zn*
This study/*Melinis repens*	Kuranda Range Road/ 6 126 ADT	1.56	2.1	12.4	10.4	4.3
Cook et al. (1994) / Taraxacum sp.	Highway, Thessaloniki, Greece	-	3.0	5.4	-	5.9

6.4.4 DTPA as a bioavailable marker: strengths and limitations

The DTPA-$CaCl_2$-HCl-TEA bioavailable solution used in this study was developed by Lindsay and Novell (1978) to examine the micronutrient fertility of soils (Lindsay and Norvell 1978; Rayment and Higginson 1992). Rayment and Higginson (1992) suggest that the solution may simulate the action of plant roots by extracting cations adsorbed onto solid phases. Recently, however, the solution has been used to assess metal bioavailability in contaminated soils (Garcia and Millan 1998).

In this study, correlation analyses were performed on the soil-DTPA and grass tissue metal values in samples obtained from the edge of the Kuranda Range Road. The data were log-normalised prior to the analyses. Samples collected 5 m from the road edge and from the background site were not included in the statistical analyses because they represent separate data sets.

Correlation coefficients (R^2 values) between soil-DTPA and stem tissue metal values in the road edge samples were very poor (Table 6-13). In fact, none of the correlations were significant at the $p<0.01$ or $p<0.05$ intervals. However, stronger positive relationships between soil-DTPA and root metal values were observed, although only in the case of Zn was the correlation significant at the $p<0.01$ or $p<0.05$ level (Table 6-13).

Positive correlations between soil-DTPA metal values and grass tissue metal levels in specimens growing on the roadside substrates were also determined in a study by Garcia and Millan (1998). In their investigation, topsoil DTPA-extractable metal values were compared with metal levels in roadside grass (*Lolium sp.*). Positive correlations ($p<0.05$) were found for Cd and Pb in addition to Zn (Garcia and Millan 1998).

Table 6-13: Correlation coefficient matrix for DTPA-extractable metal concentrations in roadside topsoils and grass tissue metal values in *M. repens* specimens growing on the roadside substrates. Correlation analyses were performed on log-normalised data. n =7. a) coefficients given by stem tissue values; and b) data produced from root tissue concentrations.

a)

Soil DTPA-extractable Cd	-0.10				
Soil DTPA-extractable Cu	-	+0.12			
Soil DTPA-extractable Pb	-	-	+0.34		
Soil DTPA-extractable Ni	-	-	-	0	
Soil DTPA-extractable Zn	-	-	-	-	+0.11
	Stem tissue Cd	Stem tissue Cu	Stem tissue Pb	Stem tissue Ni	Stem tissue Zn

b)

Soil DTPA-extractable Cd	-0.04				
Soil DTPA-extractable Cu	-	+0.17			
Soil DTPA-extractable Pb	-	-	+0.44		
Soil DTPA-extractable Ni	-	-	-	+0.16	
Soil DTPA-extractable Zn	-	-	-	-	+0.96
	Root tissue Cd	Root tissue Cu	Root tissue Pb	Root tissue Ni	Root tissue Zn

Notes: Type of correlation is indicated by +/- symbol
Correlation is significant at the $p<0.01$ level

In this study, total soil metal values and grass tissue metal concentrations showed weaker correlations in the road edge grass and topsoil samples (Table 6-14). Only Zn values in the root tissue samples were significantly positively correlated ($p<0.01$) with total soil metal levels (Table 6-14).

Thus, for the *M. repens* grass species investigated, the total soil metal levels cannot be used to infer metal bioavailability (with the exception of Zn). Garcia and Millan (1998) also noted that total soil metal levels were ineffective markers of metal availability to *Lolium sp.*, their studied grass species.

Table 6-14: Correlation coefficient matrix for total metal concentrations in roadside topsoils and grass tissue metal values in *M. repens* specimens growing on the roadside substrates. Correlation analyses were performed on log-normalised data. n =7. a) coefficients given by stem tissue values; and b) data produced from root tissue concentrations.

a)

Total soil Cd	-0.13				
Total soil Cu	-	+0.10			
Total soil Pb	-	-	+0.02		
Total soil Ni	-	-	-	-0.19	
Total soil Zn	-	-	-	-	+0.07
	Stem tissue Cd	Stem tissue Cu	Stem tissue Pb	Stem tissue Ni	Stem tissue Zn

b)

Total soil Cd	0				
Total soil Cu	-	+0.09			
Total soil Pb	-	-	+0.18		
Total soil Ni	-	-	-	+0.09	
Total soil Zn	-	-	-	-	+0.97
	Root tissue Cd	Root tissue Cu	Root tissue Pb	Root tissue Ni	Root tissue Zn

Notes: Type of correlation is indicated by +/- symbol
Correlation is significant at the $p<0.01$ level

The DTPA extractions performed in this study permitted quantification of the bioavailable metal proportions in the topsoils. The results in Table 6-5 showed higher DTPA-extractable proportions of Cu, Ni and Zn in the roadside topsoils relative to those soils collected 5 m from the road's edge and from the background site. Thus, it is concluded that the anthropogenic fraction of these particular metals in the roadside topsoils is readily bioavailable, especially Zn. Garcia and Millan (1998) found similar DTPA-extractable metal proportions (Cd = 50 %, Cu = 21 %, Pb = 23 %, Zn = 9 %) in their soils (Table 6-5). However, their research revealed no differences between DTPA-extractable metal proportions in the roadside soils as compared with their background soils (Garcia and Millan 1998).

Overall, the documented results indicate that extraction solutions have limited use to infer metal bioavailability in soils. The analyses demonstrated that certain portions of vegetation tissue, such as the root system, preferentially accumulate metals. Moreover, different metals may be concentrated in different plant portions. The DTPA solution and other bioavailable reagents cannot differentiate this partitioning.

In addition, comparison of these data with the results of other studies revealed that different species of vegetation accumulate soil-hosted metals in varying quantities. Thus, bioavailable solutions cannot reflect variable physiologies of grass and plant species.

Despite these limitations, the DTPA solution was shown to be an effective indicator of soil Cu, Pb, Ni and Zn bioavailability to the root tissue of *M. repens* specimens growing adjacent to the edge of the Kuranda Range Road. Thus, it is concluded that bioavailable solutions, such as the DTPA reagent, may be used as cost-effective, yet rudimentary markers of soil-metal bioavailability.

6.4.5 Implications of analysis of roadside *M. repens* samples

The preceding discussion has shown that very few studies have analysed metal concentrations in roadside grass species. Hence, this investigation contributes to the sparse current knowledge base on metal bioavailability to roadside grasses. The research has demonstrated that the stem and, particularly, the root tissue of grasses that grow in the immediate road edge environment have the potential to accumulate heavy metals. It is very important to gain knowledge regarding such metal accumulation in the tissue of grass species because these represent an important food source for many animals (Awofolu 2005), especially Australian native fauna. Grasses are therefore representative of a link through which metals and other contaminants may be passed up the food-chain.

6.4.6 The greenhouse experiment

The road sediments used in the greenhouse experiment exhibited similar heavy metal values to the topsoils collected adjacent to the Kuranda Range Road (Table 6-15). Furthermore, metal concentrations in the *M. repens* specimens grown in the greenhouse pots were similar to metal values detected in the roadside samples of this species (with the exception of Zn).

Table 6-15: Mean metal concentrations in road sediments used in the greenhouse experiment. n = 4 for sediment samples from the Kuranda Range Road and the Captain Cook Highway roundabouts. Median topsoil metal values adjacent to the Kuranda Range Road (n = 7) are shown for comparison.

	Cd (mg/kg)	*Cu (mg/kg)*	*Pb (mg/kg)*	*Ni (mg/kg)*	*Zn (mg/kg)*
Road sediments					
Kuranda Range Road	0.36	54.4	66.1	38.3	1330
Captain Cook Highway roundabouts	0.28	106	107	42.8	709
Roadside topsoils	0.20	61.1	97.3	28.6	729

However, Zn values were exceptionally high in the stem tissue of the *M. repens* samples grown in the road sediments (1210 mg/kg for the grasses in the Captain Cook Highway roundabout sediments and 899 mg/kg for the specimens plotted in the Kuranda Range Road sediments, Table 6-6). The stem Zn values in the greenhouse *M. repens* specimens were 3x to 5x higher than the Zn levels in the stem tissue of the roadside *M. repens* specimens. The accumulation of such high Zn values in the greenhouse *M. repens* samples implies that the Zn in the road sediments is present in a highly labile form.

DTPA extractions were performed on the road sediments to estimate the bioavailable proportions of metals hosted by these materials. The EDTA-NH_4HCO_3 solution was applied to the road sediments to validate findings of the DTPA extractions. This EDTA solution has been developed as a supplementary bioavailable indicator to the DTPA reagent to examine micronutrient availability in agricultural soils (Rayment and Higginson 1992). The EDTA solution has also been used to assess metal availability in contaminated soils (Onyatta and Huang 1998). A comparison between DTPA-extractable and EDTA-extractable metal concentrations in the road sediments revealed that the EDTA solution dissolved higher proportions of metals than the DTPA solution. EDTA-extracted metal values were approximately 1.6 times higher than DTPA-extracted metal levels (Figure 6-1).

The bioavailable proportions of each metal in the studied road sediments, as determined by the DTPA and EDTA extractions, were much lower than the bioavailable metal proportions indicated by the DTPA extractions calculated for the roadside topsoils (Table 6-7). This suggests that the metals hosted by the roadside topsoils are in a more readily available form than those hosted by the road sediments. Paradoxically though, lower concentrations of Zn were extracted by the DTPA solution from the road sediments than the roadside topsoils. This may be attributable to Zn readsorption by the road sediments during the extraction procedure. The problem of metal re-adsorption in extractions applied to road sediments was encountered in Chapter 3, where tyre rubber was concluded to be an adsorber of dissolved and suspended metals.

Overall, the results of the greenhouse experiment validated the findings of the field data. Negligible levels of Cd, Cu, Pb and Ni in the road sediments were bioavailable to the stem tissue of the potted grass specimens. Furthermore, high levels of Zn were found in the stem tissue of the greenhouse *M. repens* samples. In the root tissue of the greenhouse *M. repens* samples, Cu and Zn were detected at levels similar to those documented in the roadside *M. repens* samples.

6.5 Conclusions

The elevated Cu, Pb, Ni and Zn levels in topsoils next to the road have led to the accumulation of these metals within the roots of *M. repens* specimens growing on these substrates. Analyses of the stem tissue of these grasses indicated low Cd, Cu, Pb and Ni values. Zinc concentrations, however, were extremely elevated in the stem tissue of the roadside grasses compared with the background samples (significant at the $p<0.05$ level). In fact, Zn concentrations in stems of *M. repens* were remarkably elevated (232 mg/kg) compared with the Zn concentrations of roadside grass stems from other investigations (*Lolium sp.*, unspecified species) (Olajire and Ayodele 1997; Garcia and Millan 1998).

Root tissue metal concentrations were generally higher than stem metal values in the *M. repens* samples analysed in this study. Zinc, however, was an exception to this. Stem Zn levels were higher than root Zn values in all grass analysed. By comparison, median Cu, Pb and Zn concentrations were elevated in the roots of the roadside grass compared with the roots of the background specimens.

The DTPA extraction solution was found to be a rudimentary indicator of soil metal availability to the root tissue of *M. repens* collected from the edge of the Kuranda Range Road. Results of the DTPA extractions on the topsoil samples revealed that the anthropogenic fractions of Cu, Ni and Zn in soils next to the road edge were readily bioavailable.

Results from the greenhouse experiment showed that heavy metals are also available to grass specimens that grow in road sediments. Zinc was detected in much higher concentrations than the other metals in the stem and root tissue of *M. repens* specimens. Metal concentrations in the tissue of the greenhouse *M. repens* samples were similar to the metal values detected in the field samples collected adjacent to the Kuranda Range Road. Results of extractions performed on the road sediment samples revealed that the EDTA bioavailable solution is more aggressive in dissolving metal contaminants from these sediments than the DTPA solution.

The results in this chapter indicated that there is an increased uptake of metals, notably Cu, Pb, Ni and Zn, by roots of *M. repens* grasses growing next to the Kuranda Range Road. This grass represents a link in the local food-chain. Consequently, traffic-derived metals may be transferred into other organisms that feed on these grasses. Even though metal enrichment was documented to be restricted next to the road edge, grazing on these grasses by marsupials, worms and insects cannot be discounted. As such, there is potential for these metals to be incorporated into the local food-chain. This is particularly true for Zn, which was detected in very high levels in the stem tissue of the *M. repens* grass analysed in this study. Further research is needed to verify this hypothesis. Such research could include: a) a study into the feeding patterns of local herbivores; and b) an investigation into metal contamination in other grass species growing adjacent to the road.

Chapter 7 Remediation of road runoff waters

7.1 Introduction

The Queensland Department of Main Roads plans to upgrade the existing Kuranda Range Road from two lanes to four, in order to accommodate an increase in traffic volume in the region (Queensland Department of Main Roads 2004a). Therefore, measures are required to ensure that the increased traffic does not cause negative environmental impacts to the surrounding World Heritage-listed landscape. Results presented in Chapters 5 and 6 demonstrated that traffic-derived metal contaminants are being dispersed over roadside soils and into surface waters adjacent to the existing Kuranda Range Road. Moreover, it was shown in Chapter 6 that Cu, Pb, Ni and Zn are accumulating within the tissue of a grass species (*M. repens*) growing along the road edge. Consequently, a study is warranted into methods that limit the transport of traffic-derived metal contaminants from their source (i.e. motor vehicles, road infrastructure and road paving materials) to adjoining environments during the road upgrade.

Additional to dissolved metals, road runoff waters host various other types of contaminants, including litter and suspended solids (Allison et al. 1997; Wong et al. 2000). Road runoff waters mobilise high concentrations of all contaminants during rainfall events. Hence, various primary, secondary and tertiary treatment measures have been emplaced in roadside environments to mitigate against the dispersion of these pollutants (Wong et al. 2000). Treatment options have varied from at-source technologies (e.g. gross pollutant traps), to in-line remediation (e.g. porous paving) through to end-point treatment measures (e.g. constructed wetlands) (McRobert and Sheridan 2001).

Dissolved contaminants, including heavy metals, are often identified as the contaminants of greatest concern in road runoff waters. This is due to their enhanced lability and bioavailability (Herngren et al. 2005). Thus, numerous studies have researched remediation options to restrict the dispersal of metal contaminants from road surfaces into adjoining environments (e.g. Barrett et al. 1995; Lau et al. 2000; Pontier et al. 2001; Toomey et al. 2003). Furthermore, other investigations have examined the adsorptive capacities of several types of materials (e.g. mulches, modified clays and synthetic zeolite) to remove dissolved metals from laboratory leachates spiked with dissolved metal salts (Pitcher et al. 2004; Jang et al. 2005; Krikorian and Martin 2005). However, these experiments have not examined the kinetics of metal removal from road sediment leachates or road runoff waters. An understanding of the kinetics of the removal rates exhibited by the adsorptive materials is considered to be very important, particularly for wet-dry tropical locations. In these environments, remediation materials must rapidly remove contaminants from ‘first flush’ road runoff waters. Moreover, remediation studies should focus on the removal of all metal species (e.g. ionic species, complexes and colloids) in road runoff waters. Despite this, previous adsorption experiments have been restricted to the use of metal salt solutions (e.g. nitrate and acetate salts, Krikorian and Martin 2005; nitrate salts, Jang et al. 2005) to simulate runoff waters. In fact, even studies which have examined urban runoff waters have added metal nitrate salts to stormwater solution (e.g. Pitcher et al. 2004). The limitation of using such solutions in remediation experiments is pointed out by Krikorian and Martin (2005) who state “one cannot depend on heavy metal ions being present as salts”. Thus, there is clearly the potential to further explore metal removal from road sediment leachates and runoff waters.

Overall, the major aims of this chapter are to: a) evaluate remediation measures for road runoff waters on the upgraded Kuranda Range Road; and b) assess the removal efficiency of zeolite, bentonite and mushroom compost to adsorb dissolved metals from road sediment leachates. The first aim involves the application of a selection methodology for the Kuranda Range Road Upgrade. The selection methodology is formulated by examining existing technologies for remediating runoff waters. The second aim was pursued via laboratory experiments.

7.2 Treatment options: a technical review

7.2.1 Pollutants in road runoff waters

Various sizes of pollutants have been identified in storm and road runoff waters (McRobert and Sheridan 2001). Large pieces of debris, greater than 5 millimetres in diameter, are referred to as gross pollutants (Allison et al. 1997). Examples of gross pollutants include litter and vegetation (Allison et al. 1997). Gross pollutants pose a threat to wildlife as well as visually blighting impacted landscapes (Allison et al. 1997).

Table 7-1: Pollutants in road runoff waters and their common grain size (from Melbourne Water 2005)

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Road runoff waters also mobilise suspended solids, which commonly comprise eroded soil, sediment and organic particles which themselves carry attached contaminants (e.g. heavy metals) via adsorption (Wong et al. 2000). Finally, dissolved pollutants constitute the smallest and most labile category of contaminants in road runoff waters. Dissolved pollutants include but are not limited to heavy metals, nitrates, phosphates and pesticides (Wong et al. 2000). Dissolved materials have been identified by Herngren et al. (2005) as the most toxic contaminants in urban runoff waters, owing to their high lability. Furthermore, dissolved metals are non-degradable (Herngren et al. 2005).

Dissolved metal contaminants are the focus of the experimental section of this chapter. Nonetheless, larger suspended solids and gross pollutants must also be considered when proposing a complete remediation sequence or ‘treatment train’ to improve the quality of road runoff waters (Melbourne Water, 2005).

7.2.2 Existing remediation technologies

Several technologies have been developed to remove gross pollutants from road runoff waters. Remediation systems can target contaminants: a) at their source (i.e. at-source pollutant traps [ASPTs]); b) within the stormwater drainage network (i.e. in-line pollutant traps); or c) at locations where storm and road runoff waters are ultimately received (i.e. end-point pollutant traps) (McRobert and Sheridan 2001). Allison et al. (1997) identify six types of devices that are being extensively used in Australia to trap gross pollutants (Table 7-2).

Once the gross pollutants have been removed from storm or road runoff waters, it is necessary to address suspended and dissolved contaminants (McRobert and Sheridan 2001). Previous studies have shown that secondary and tertiary technologies to remove suspended and dissolved contaminants from runoff waters are often integrated into a single remediation system (Table 7-2).

Constructed wetlands, sediment detention ponds, sediment tanks, grassy swales/roadside buffer strips, peat filtration systems and biofilters all possess the requisite physical, chemical and biological conditions to trap suspended solids as well as offering adsorption properties to sequester dissolved pollutants (Barrett et al. 1995; Dierkes and Geiger 1999; Lau et al. 2000; Pontier et al. 2001; Shutes et al. 2001; Aldheimer and Bennerstedt 2003; Toomey et al. 2003; Zhou et al. 2003; Han et al. 2005; Starzec et al. 2005). These remediation systems are commonly incorporated into drainage networks away from road edges; that is, they are either in-line or end-point devices. The reported success of these pollutant traps are summarised forthwith.

Table 7-2: List of current primary, secondary and tertiary treatment devices for road runoff waters.

Level of treatment	System name	Description	Reference
Primary	Side Entry Pit Trap (SEPT)	• Basket inserted below drain entrances. Pollutants are captured in sieve mesh (5 mm – 20 mm).	Allison et al. (1997)
Primary	Trash Rack	• Vertical or horizontal steel bars 40 mm – 100 mm apart. Fitted into large stormwater channels (10 m wide).	Allison et al. (1997)
Primary	Litter Control Device (LCD)	• Similar to SEPT. Inserted at inlet of stormwater pipe.	Allison et al. (1997)
Primary	Continuous Deflective Separation (CDS)	• Helix structure. Keeps runoff waters in motion, trapping larger debris. Inserted in drains.	Allison et al. (1997)
Primary	Gross Pollutant Trap (GPT)	• Large-scale trash racks inserted into stormwater weirs.	Allison et al. (1997)
Primary	Floating Debris Trap (FDT)	• Netted, floating bunds used in surface water bodies	Allison et al. (1997)
Secondary and tertiary	Constructed wetland	• Constructed surface water body with encouraged growth of vegetative communities. Designed to capture storm and road runoff waters.	Toomey et al. (2003)
Secondary and tertiary	Sediment detention pond	• Surface water bodies with no encouraged establishment of vegetative communities. Designed to capture storm and road runoff waters.	Lee et al. (1997)
Secondary and tertiary	Sediment tank	• Containers inserted into road drainage systems.	Aldheimer and Bennerstedt (2003)
Secondary and tertiary	Grassy swale	• Strips of soil on which growth of grasses is established.	Dierkes and Geiger (1999)
Secondary and tertiary	Peat filtration system	• Two-way container comprising a sand and peat layer. Inserted into drainage culvert.	Zhou et al. (2003)
Secondary and tertiary	Biofilter	• Culture of microorganisms growing on granular materials which can be incorporated into road drainage systems.	Lau et al. (2000)
Tertiary (limited for secondary)	Adsorptive materials	• Silicates, clays, organic materials, mine slag, synthesised compounds which are able to adsorb dissolved contaminants	Pitcher et al. (2004), Jang et al. (2005), Kriokorian and Martin (2005)

Constructed linear wetlands have been trialled by a number of researchers to remove sediments and dissolved contaminants from storm and road runoff waters. For example, Toomey et al. (2003) suggested that linear wetlands incorporated adjacent to the major road servicing the Port of Brisbane, Australia, were capable of treating runoff waters from the road to ‘a high standard’. However, no quantitative data were presented in the study. Other research by Pontier et al. (2001) and Shutes et al. (2001) demonstrated that constructed wetlands are able to remove large quantities of suspended sediments as well as dissolved metal contaminants from road runoff waters.

Roadside detention or sediment ponds are similar to wetlands, with the difference being that there is no effort to encourage vegetative growth in detention ponds (Lee et al. 1997). Lee et al. (1997) and Starzec et al. (2005) reported high removal efficiencies for sediments and dissolved contaminants by roadside detention ponds.

The ability of a sediment holding tank to sequester suspended and dissolved contaminants from road runoff waters was examined by Aldheimer and Bennerstedt (2003). The sediment holding tank removed, on average, 84 % of suspended sediments entering the stormwater system (Aldheimer and Bennerstedt 2003). High levels (60 to 80 %) of dissolved heavy metals (Cu, Pb and Zn) were also sequestered from the runoff waters by the sediments in the holding tank (Aldheimer and Bennerstedt 2003).

Other investigations have examined the effectiveness of simple grass swales and embankments to adsorb traffic-derived metal contaminants from road runoff waters. For example, Dierkes and Geiger (1999) studied Cd, Cu, Pb and Zn removal from road runoff waters by greened embankments. Their research did not reveal any notable remediation qualities of the embankments adjacent to the road. Furthermore, the inability of vegetative filter strips to trap very fine sediment particles, which host the most labile fraction of metal contaminants, was encountered by Han et al. (2005). Barrett et al. (1995) also examined the effectiveness of grass swales to capture Cu, Pb and Zn from road runoff waters. In contrast to other studies (e.g. Dierkes and Geiger 1999; Han et al. 2005), Barrett et al. (1995) concluded that the presence of a grassy buffer zone between the lanes of and beside the highway constituted an extremely effective method for trapping metals carried by road runoff waters (Barrett et al. 1995).

A number of other studies have focused on technologies which remediate road runoff waters at the point of discharge from the road (i.e. at-source pollutant traps). For example, a peat filtration system was trialled by Zhou et al. (2003) to remove sediments and dissolved materials from road runoff waters. Their study was conducted in a karst landscape and aimed to restrict the dispersal of contaminants into groundwater. Results of their examination showed the peat filter barrier was an effective material in lowering dissolved Cu and Zn concentrations as well as total suspended solid levels in the road runoff waters (Zhou et al. 2003). Furthermore, Lau et al. (2000) demonstrated that biofilters (consisting of microorganisms growing on granular materials) installed in drainage culverts are effective secondary and tertiary treatment measures.

Fewer investigations have focused solely on removal methods for dissolved contaminants in storm and road runoff waters. The studies have largely focused on the effectiveness of adsorptive materials to reduce metal concentrations in laboratory solutions of distilled water and road runoff waters with added dissolved metal salts. For example, the capacity of mulches to adsorb dissolved heavy metals from contaminated solution was examined by Jang et al. (2005). The results of their investigation showed that hardwood bark mulch was extremely effective in reducing dissolved Cu, Pb and Zn levels. Moreover, the mulch incurred negligible pH changes in the solution, which was viewed to be a critical chemical process in optimising metal adsorption by the mulches (Jang et al. 2005). Krikorian and Martin (2005) showed that clays modified with organic catalysts are capable of adsorbing vast amounts of metals from laboratory solutions consisting of distilled water and dissolved metal salts. In addition, Pitcher et al. (2004) demonstrated that synthetic zeolite is able to remove almost the entire reservoir of dissolved metals from spiked solutions.

7.2.3 Commercially-available remediation devices

A number of the treatment technologies described in Section 7.2.2 have been developed into commercial remediation devices. Allison et al. (1997) report that Side Entry Pit Traps (SEPTs), Trash Racks, Litter Control Devices (LCDs), Continuous Deflective Separation (CDS) units, Gross Pollutant Traps (GPTs), and

Floating Debris Traps (FDTs) have all been used extensively by councils in Australia to remediate gross pollutants from storm and road runoff waters.

Outside Australia, numerous other commercial devices have been developed to target gross pollutants as well as suspended solids in urban runoff waters. Some examples include the BioSTORM™ (developed by BIO-MICROBICS Inc.); the Downstream Defender® (designed and created by Hydro International); the EnviroPod^{TM}, the StormFilter, the StormScreen® (all produced by Stormwater Management Inc.); the SPI system (engineered by SPILL Station Australia Pty Ltd); and the Vortechs®, VortSentry^{TM}, and VortCapture^{TM} (all developed by Vortechnics®). Moreover, the StormFilter has been shown to be an effective tertiary treatment device (Noling and Kellems) Another device of Stormwater Management Inc., the Electrocoagulation System™, also removes dissolved metals from runoff waters through induced precipitation and flocculation (Stormwater Management Inc. 2005b).

Figure 7-1: Two examples of commercially-available storm and road runoff water treatment devices: a) the EnviroPod^{TM} Filter (Stormwater Management Inc. 2005a); and b) the SPI system (SPILL Station Australia 2005).

7.3 Selection methodology for the Kuranda Range Road Upgrade

7.3.1 Proposed road upgrade

The Queensland Department of Main Roads (Qld Main Roads) intends to upgrade of the existing Kuranda Range Road from two lanes to four (Queensland Department of Main Roads 2004c). The proposed timeframe for the upgrade completion is 10 years, although no specific commencement date has been identified for the project (Queensland Department of Main Roads 2004e). An assessment of the road upgrade route by Qld Main Roads has established that there is the need to consider the quality of road runoff waters in certain locations, which may impact on adjoining catchments in WTWHA-listed rainforest (Queensland Department of Main Roads 2004d).

7.3.2 Planning framework for remediation measures

Any remediation measure for the treatment of storm or road runoff waters must be based on a planning framework (Ellis et al. 2004). Ellis et al. (2004) propose a four-criteria framework for the development of a sustainable urban drainage system (SUDS) (Figure 7-2).

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Figure 7-2: Key factors in the design of a sustainable urban drainage system (from Ellis et al. 2004).

The Kuranda Range Road traverses a landscape of environmental significance with World Heritage status. Thus, the focus on the road upgrade will be on mitigating negative environmental impacts. However, the road is also closely linked with adjoining residential areas (in Kuranda and Smithfield). Moreover, economic benefits and technical proficiency of any remediation measures designed for roads are critical objectives. Thus, strong weighting must be given to all four criteria in Ellis et al.'s (2004) planning framework when designing remediation measures for the Kuranda Range Road Upgrade.

7.3.3 Road runoff water quality objectives

Figure 7-3 shows the two major catchments that receive runoff waters from the Kuranda Range Road: Streets Creek and Avondale Creek. Queensland Main Roads have identified these two permanent streams as the most sensitive water bodies adjacent to the road (Queensland Department of Main Roads 2004d). Hence, a major aim of Qld Main Roads is to stop contaminants from reaching these creek systems (Queensland Department of Main Roads 2004d). In order to achieve this goal, treatment of runoff waters at each creek intersection along the upgraded road will be necessary as numerous ephemeral creeks feed into the two main catchments (Figure 7-3).

A total of 24 ephemeral and perennial creek crossings are identified along the route of the Kuranda Range Road Upgrade (Figure 7-3). During the 'wet season', contaminants dispersed into the ephemeral creeks will be delivered to the main catchments in the area. Thus, treatment of road runoff waters should not simply be restricted to the two locations where the Kuranda Range Road crosses the perennial branches of Streets Creek and Avondale Creek (Figure 7-3). Indeed, each creek/road intersection must be addressed.

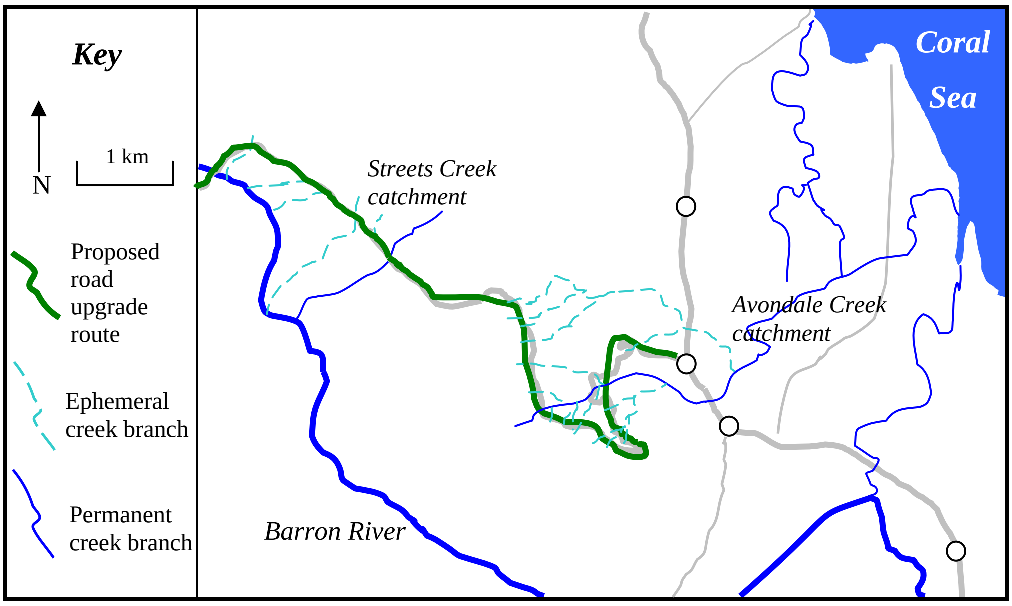

Figure 7-3: Proposed upgrade route of the Kuranda Range Road showing the numerous intersections of the two main catchments in the area: Streets Creek and Avondale Creek.

7.3.4 Criteria in developing treatment processes

The aim of this section is to evaluate remediation measures for road runoff waters on the Kuranda Range Road Upgrade. The methodology for evaluating the measures is based on accepted procedures recommended by Melbourne Water (2005). Specifically, Melbourne Water (2005) lists six steps that need to be considered in designing and implementing a suitable treatment program for storm and road runoff waters for any given location (Table 7-3).

Table 7-3: Key steps in developing and implementing a remediation system for storm and road runoff waters (from Melbourne Water 2005).

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7.3.4.1 Step 1 Determining the treatment objectives

The first step (Table 7-3) in Melbourne Water's (2005) selection procedure is to identify the pollutants of concern and the degree of removal required. Gross pollutants, suspended solids, and dissolved materials are commonly-identified pollutants in road runoff waters (McRobert and Sheridan 2001). Hence, remediation of all of these pollutants is required for a finalised treatment plan for the Kuranda Range Road Upgrade. Of particular concern are dissolved heavy metal contaminants which are highly mobile. Moreover, heavy metals do not degrade in the environment and are commonly toxic to organisms in low concentrations (Herngren et al. 2005).

The degree of pollutant removal required for the Kuranda Range Road runoff waters can be initially assessed by reference to ANZECC Guidelines (2000). McRobert and Sheridan (1997) state that the ANZECC Guidelines "provide recommendations to help managers of road assets and other contributors to water quality pollution take actions to maintain environmental values in waterways". However, McRobert and Sheridan (1997) also note that the guidelines should not be used as standards, rather as monitoring and investigation triggers. In the case of the Kuranda Range Road Upgrade, the most stringent level (the 99 % Protection Level for Freshwater Ecosystems) is examined as the threshold interval, considering the ecological significance of the adjoining WTWHA rainforest (Queensland Department of Main Roads 2004d). Investigation levels for several pollutants in freshwater systems are shown in Table 7-4. The table indicates a range of values for various contaminants established by ANZECC (2000) and Australian Standards (Wong et al. 2000). While established guidelines are in place for suspended and dissolved pollutants, there is no formal protocol for the monitoring of gross pollutants in urban runoff waters (Wong et al. 2000).

Table 7-4: Threshold values for various pollutants in storm and road runoff waters. *Refers to Trigger Values for Freshwater Ecosystems, 99 % Protection Level. Australian Standards for runoff waters are from Wong et al. (2000). NE = none established, NM = not measured. Refer to Appendix A for ID for 'first flush' road runoff water samples collected in November 2004.

	ANZECC Guidelines (µg/L)*	**Australian Standards for runoff waters (µg/L)**	**'First flush' values in Kuranda Range Road runoff waters, collected in Nov. 04 (µg/L)**	**Background stream values (µg/L)**
Gross pollutants	NE	-	NM	NM
TSS	NE	<10 % change	NM	NM
Turbidity	2 – 15 NTU	-	NM	NM
Cd	0.06	0.2 – 2	≤0.05	≤0.05
Cu	1	2 – 5	13.5	0.81
Pb	1	1 – 5	2.5	0.1
Ni	8	15	6.1	0.27
Zn	2.4	5 – 50	235	15.6
TN	NE	<10 – 100	NM	NM
TP	NE	<100 – 750	NM	NM

Table 7-4 also lists 'first flush' metal concentration data for road runoff waters on the Kuranda Range Road. The table indicates that the median Cu, Pb and Zn concentrations in the 'first flush' road runoff water samples acquired in November 2004 were all higher than their respective ANZECC (2000) threshold values (Freshwater Ecosystems, 99 % Protection Level) as well as the Australian Standards. However, data in Table 7-4 reveal that Zn values in local background streams also exceeded the ANZECC (2000) threshold levels (Freshwater Ecosystems, 99 % Protection Level). Hence, it is proposed that metal concentrations in local background streams provide a more suitable measure of baseline metal values than investigation levels and standards. Consequently, the local background stream metal concentrations are set as target levels for the remediation of road runoff waters on the upgraded Kuranda Range Road. Table 7-5 presents reduction factors required for metal values in 'first flush' road runoff waters to meet background stream levels. The reduction factors are based on data from this study.

Table 7-5: Reduction factors required for metal values in road runoff waters to meet local background stream metal values.

	Reduction factors required to meet local stream values	**Background stream water values (µg/L)**
	'First flush' road runoff waters	
Cd	0	≤0.05
Cu	17x	0.81
Pb	25x	0.1
Ni	2x	0.27
Zn	15x	15.6

7.3.4.2 Step 2 – Developing a 'treatment train'

The second step in Melbourne Water's (2005) remediation selection process (Table 7-3) demands the development of a 'treatment train' to address the targeted pollutants. Gross pollutants, sediments and dissolved materials (including metals) are all listed as contaminants of concern by Qld Main Roads (Queensland Department of Main Roads 2004d). Thus, a 'treatment train' incorporating primary, secondary and tertiary remediation measures is deemed necessary for the Kuranda Range Road Upgrade. The form of remediation will be influenced by the design of the road upgrade. Figure 7-4 illustrates a generic bridge structure for creek crossings on the Kuranda Range Road Upgrade. The figure shows that there is an extremely short distance between the pollutant source (i.e. the road surface and edge) and the sensitive receiving catchments (i.e. streams which drain into Streets Creek and Avondale Creek).

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Figure 7-4: A common bridge structure on the Kuranda Range Road Upgrade (over Avondale Creek), showing the close proximity of the drainage point and the receiving catchment waters (Queensland Department of Main Roads 2004b).

The proximity of the drainage points on the Kuranda Range Road to the receiving stream catchments suggests that there is insufficient working space for the implementation of large end-point or in-line remediation measures adjacent to these bridge structures. Instead, at-source pollutant control (i.e. on the bridge) will likely be the most effective form of primary, secondary and tertiary pollutant attenuation on the road upgrade.

7.3.4.3 Step 3 – Identifying the site's characteristics

The third step in the selection process outlined by Melbourne Water (2005) (Table 7-3) involves an assessment of the study site, focusing on potential site constraints. Strategies to limit the dispersal of contaminants in storm and road runoff waters need to take account of site-specific climatic and geographical characteristics (Pitt et al. 1995). Moreover, site characteristics may diminish the effectiveness of particular remediation measures. The use of exclusion criteria has been identified as a critical process in designing urban water treatment systems (Ellis et al. 2004). These criteria deem certain treatment options unsuitable for particular locations and include factors such as site gradient, land-use and water table height (Ellis et al. 2004). Ellis et al. (2004) have developed an exclusion criteria1 remediation option matrix, which enables planners to assess the suitability of particular treatment options (Table 7-6).

Table 7-6: Site constraint/treatment option matrix for road and storm water treatment design (from Ellis et al. 2004).

The 'land-use' criteria in Ellis et al.’s (2004) matrix is a limiting factor for the Kuranda Range Road Upgrade. The land adjacent to the Kuranda Range Road is of high conservation value, as the road traverses WTWHA-listed rainforest (Figure

7-5). Moreover, the plan for the proposed upgrade works stipulates minimal disturbance to the immediate roadside environment (Queensland Department of Main Roads 2004a). Hence, diversion of road runoff waters into in-line remediation measures adjacent to bridge structures on the Kuranda Range Road Upgrade cannot be achieved. Additionally, the matrix clearly shows that the effectiveness of grass swales or filter strips adjacent to the road will be compromised by the steep gradient of the terrain (Table 7-6).

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Figure 7-5: Plan for upgraded route of Kuranda Range Road. The section of road depicted is the Henry Ross Lookout, near the top of the range (Queensland Department of Main Roads 2004b).

As discussed previously, the drainage points on the road upgrade will discharge runoff waters directly into adjoining sensitive catchments during the ‘wet season’. These runoff waters should therefore be treated before they are discharged into the sensitive catchments. Queensland Main Roads stress that the objective of the water quality program for the road upgrade is to “focus on protecting local aquatic ecosystems” (Queensland Department of Main Roads 2004d). Thus, the implementation of end-point remediation measures (such as a constructed wetland or a trash rack weir) at the base of the Macalister Range would not mitigate upstream impacts.

The heavy seasonal rainfall in the region is another factor that has to be considered in designing remediation measures for the Kuranda Range Road Upgrade. Any remediation measure in the wet-dry tropics would need to accommodate flows of extremely large volumes of 'first flush' waters that pass over the road at the onset of the 'wet season'. Systems such as detention ponds, which do not have flow bypass devices, would therefore be unsuitable for the road upgrade, as they would be prone to flooding during periods of heavy rainfall.

In summary, the Macalister Range poses several physical (e.g. gradient), environmental (e.g. land use) and climatic (e.g. rainfall) limitations on remediation measures for the Kuranda Range Road Upgrade. Thus, the finalised remediation measure devised for the road needs to take into account these obstacles.

7.3.4.4 Step 4 – Short-listing potential treatment options

Consideration of the fourth step in the selection process (Table 7-3) requires a short-listing of all potential treatment options for the Kuranda Range Road Upgrade. Based on discussions in Sections 7.3.4.1 to 7.3.4.3, ASPTs are recognised as the most effective method for pollutant attenuation on the road upgrade. Various treatment technologies for the Kuranda Range Road Upgrade are short-listed and described in Table 7-7. Examples of commercially-available devices are presented where known.

Table 7-7: Short-list of ASPT remediation devices for the Kuranda Range Road Upgrade.

Treatment level	Short-listed options		Description
Primary	General treatment technologies	SEPT	Baskets with trapping mesh.
		Trash rack	Vertical or horizontal trapping bars over drainage culverts.
		CDS	Helical device to keep water in motion while separating litter and debris into containment chamber.
	Commercially patented devices	Baramy	Comprises pollutant holding shelf opened by hydraulically activated valve.
		Diston	Litter basket, floating pollutant separator and trash rack.
		Litterguard	Boom-operated litter trap.
		Ecosol RSF 4000	Litter-collection basket with flow divert function.
		Ski-Jump	Trash rack and collection chamber.
		VortCapture™	Uses a CDS system to retain pollutants >5mm in sump.
Primary/ secondary	Commercially patented devices	BioSTORM™	Trash collector, floating debris trap and fine sediment filter.
		EnviroPod™	Runoff waters are directed through a coarse mesh and then through a filter to trap finer sediments.
		Hydroscreen	Consists of a trash rack coupled with filter.
		StormScreen®	Incorporates a series of fine filter cartridges housed in a sediment catching basin.
		SPI system	Comprises a flow-direction plate, gross pollutant trap, hydrocarbon filter and mounting arms.
		Vortechs®	Comprises a baffle wall and grit collection chamber whilst allowing bypass of runoff waters at high flow rates.
		VortSentry™	Employs a CDS system and a sediment filter.
Secondary	Commercially patented devices	Aqua–Filter	Consists of a filtration chamber.
		Downstream Defender®	Container with central sump able to retain pollutants as water is kept in motion in outer chamber.
		VortFilter™	Gravitational separation of coarse sediments and physical filtration of fine sediments down to 7 µm.
Secondary/ tertiary	General treatment technologies	Peat filtration system	Consists of an open ended container with a peat layer underlying a sand and gravel layer. The sand and gravel trap coarse sediments, while the peat layer is capable of adsorbing dissolved materials.
		Precipitation basin	Comprises an open ended container filled with limestone gravel. The limestone causes a pH increase in the incoming runoff water and results in the precipitation of dissolved metals.
		Biofilter	Granular surface coated with culture of microorganisms.
	Commercially patented devices	StormFilter	Comprises a cartridge consisting of perlite, zeolite, activated carbon and compressed mulch media.
		Electrocoagulation System™	Consists of electrolytic cells which, when charged, cause flocculation of colloids and precipitation of metals due to formation of oxides

7.3.4.5 Step 5 – Comparing the treatment options

Step 5 in Melbourne Water's (2005) selection process requires a comparison of the effectiveness of the short-listed options (Table 7-3). Effectiveness in this study is based on pollutant removal efficiency as well as cost.

All listed primary treatment options in Table 7-7 have been shown to exhibit high pollutant removal capabilities. For example, the Continuous Deflective Separation device (CDS) has been reported to achieve 100 % removal of gross pollutants from storm and road runoff waters (Allison et al. 1997). However, the construction and maintenance of such systems are costly (Allison et al. 1997). In comparison, simple trash rack devices are more cost-effective (Allison et al. 1997). Additionally, these systems are also very efficient in removing vast amounts (up to 85 %) of gross pollutants from road runoff waters (Allison et al. 1997).

The numerous commercially-available secondary ASPT devices listed in Table 7-7 have shown variable performance results. For example, the Aqua-Filter system reportedly achieves a 98 % removal efficiency for suspended sediments (< 75 μm) in urban runoff waters (Washington State Department of Ecology 2005c). Moreover, the device attains a greater than 80 % removal rate for Cu and Zn (Washington State Department of Ecology 2005c). However, it is not clear whether this reported efficiency value was for particulate or dissolved metals.

The Downstream Defender® demonstrated a lower sediment removal capacity than the Aqua-Filter system (Washington State Department of Ecology 2005a). Approximately 80 % of suspended sediments (<125 μm) were removed by the Downstream Defender® in the Washington State Department of Ecology's assessment (2005). By comparison, the Auckland City Council revealed that the EnviroPod™ can remove 100 % of sediments (>100 μm) in road runoff waters (Butler et al. 2003). Despite this, the EnviroPod™ yielded a much lower rate of effectiveness (18 % removal efficiency) for sediments <100 μm (Butler et al. 2003). In another study on the performance of the EnviroPod™ by the Hornsby Shire Council, a 50 % reduction in particulate metal (Cu, Pb and Zn) concentrations was observed (Hornsby Shire Council 2004).

The Vortechs® system reportedly removes approximately 80 % of sediments (<100 μm) in stormwater (Washington State Department of Ecology 2005b). More effective in removing fine sediments is the VortFilter™, which has been shown to capture 85 % of suspended sediment (<35 μm) from urban runoff waters (Vortechnics Inc. 2004). In comparison, the VortSentry™ has demonstrated a sediment (total suspended load) removal efficiency of ca. 60 % (Allen).

The tertiary ASPT treatment systems listed in Table 7-7 have also been trialled, with variable reported pollutant removal efficiencies. For example, a peat filtration system examined by Zhou et al. (2003) adsorbed approximately 85 % of dissolved Zn from road runoff waters. Moreover, a biofilter assessed by Lau et al. (2000) removed 90 % of dissolved Pb and Zn from road runoff waters.

Additionally, two tertiary ASPT devices are commercially-available: the Electrocoagulation System™; and the StormFilter. The Electrocoagulation System™ has been reported to achieve a 100 % "cleaning efficiency" for water, although no specific details of the treatment were given (Stormwater Management Inc. 2005b). By comparison, the StormFilter was shown to remove 32 % of dissolved Cu and 48 % of dissolved Zn from 'first flush' runoff waters in a shipping yard in the United States (Noling and Kellems). Lenhart et al. demonstrated a maximum Cu removal of 92 % and a maximum Zn removal efficiency of 64 % in a series of runoff treatment studies in industrial locations in the United States (Lenhart et al.). The costs of some of the various short-listed commercial devices are shown in Table 7-8.

Table 7-8: Costs of the short-listed commercially-available remediation devices.

Device	Cost per unit (Aus $)	Maintenance costs (Aus $)
Baramy	15000 – 40000 (Taylor 2005)	12 per ha per month
Ecosol RSF 4000	4000 –12000 (Taylor 2005)	12 per ha per month
VortCapture™	35000 (Burk 2005)	
EnviroPod™	440 – 620 (Taylor 2005)	200 per year
SPI system	965 (1 m x 1 m) (Hancock 2005)	
Vortechs®	34000 (Taylor 2005)	
VortSentry™	27000 (Burk 2005)	
Downstream Defender®	12000 – 36000 (Taylor 2005)	20 per ha per month
VortFilter™	47000 (Burk 2005)	
StormFilter	15000 – 200000 (USEPA 2005)	

7.3.4.6 Step 6 – Finalising the design for the treatment system

Overall, few treatment options are suitable for the Kuranda Range Road Upgrade. While most of the short-listed primary treatment options have shown high removal efficiency rates for their targeted pollutants, the cost of the commercially-available devices are quite high (Table 7-8). Moreover, the cost per unit for each device would have to be factored in for each location on the road upgrade where remediation is needed. Figure 7-3 showed that 24 stream crossing sites on the Kuranda Range Road Upgrade will require the implementation of a remediation system. Thus, the purchase of the listed commercially-available ASPTs is not economically-viable for the road upgrade. Instead, cheaper trash rack-type devices, consisting of a grill mesh, are considered to be the most effective primary form of pollutant removal for the Kuranda Range Road Upgrade. Trash racks can be inserted into drainage culverts on the 'critical points' of the road (i.e. those locations where runoff waters drain into the Streets Creek and Avondale Creek catchments).

Commercial devices with secondary treatment capabilities (e.g. the EnviroPod™ and the SPI system) are also expensive (Table 7-8). However, the filtration technologies used in these systems can be applied to more economical treatment strategies. For instance, a series of sand and gravel filters could be placed within drainage culverts on bridges of the Kuranda Range Road Upgrade. Sand and gravel filters were shown to be an effective form of secondary treatment of road runoff waters by Zhou et al. (2003).

Finally, tertiary treatment options need to be incorporated into the remediation system for the Kuranda Range Road Upgrade. The implementation of commercially-available treatment devices is one option for tertiary treatment on the upgraded road. The Electrocoagulation System™ and the StormFilter have both been reported to achieve high capture rates for dissolved pollutants, including metals. However, these systems are very expensive, even more so than the commercially-available primary and secondary treatment devices (Table 7-8). Thus, additional tertiary treatment options need to be considered for the Kuranda Range Road Upgrade. Biofilters, adsorptive layers (peat) and precipitation trenches have all been reported to be successful tertiary pollutant removal measures (Lau et al.

2000; USEPA 2003; Zhou et al. 2003). Their reported metal capture rates (90 % Pb and Zn for the biofilter, and 85 % Zn for the peat layer) have the potential to reduce ‘first flush’ road runoff water metal values on the Kuranda Range Road Upgrade to a degree that complies with local background stream levels. Moreover, these technologies are much cheaper than the commercial devices listed in Table 7-8. Thus, biofiltration, adsorption and precipitation are alternative tertiary treatment options for the Kuranda Range Road Upgrade. Adsorptive materials (such as peat e.g. Zhou et al. 2003), biofilters (e.g. microorganism coatings on granular materials, Lau et al. 2000) and precipitation-inducing minerals (e.g. lime pebbles, USEPA 2003) may be placed onto sand filter beds which can thereby achieve tertiary treatment of contaminated road runoff waters. Proposed treatment options for the Kuranda Range Road Upgrade are presented in Table 7-9. The focus of the remediation system is on at-source treatment via the use of ASPTs.

Table 7-9: Proposed 'treatment train' for the Kuranda Range Road Upgrade.

Pollutants and particle size	**Treatment Measures**		
	Primary	**Secondary**	**Tertiary**
Gross pollutants (<5mm)	ASPT– screening of pollutants at the road edge in drainage culvert entrances.		
Coarse sediment (0.5 – 5mm)		ASPT – sediment filter bed	
Medium sediment (62 µm – 0.5 mm)			
Fine sediments (<62 µm)			ASPT – Commercial device (e.g. StormFilter) OR sand bed with biofilter/precipitation /adsorption materials
Attached pollutants			
Dissolved pollutants (<0.45 µm)			

7.3.5 Recommendations and considerations for the finalised treatment measures

The proposed treatment measures for the Kuranda Range Road Upgrade are only suggested options (Table 7-9). The development of an effective remediation program for the road will depend on further work; namely field testing of the selected measures on the studied road. It is envisaged that the most challenging problem for devising remediation measures for the road upgrade will be coping with the vast volumes of water that pass over road surfaces during the ‘wet season’. Thus, the chosen remediation method will need to accommodate immense volumes of runoff waters without clogging and flooding the road.

Secondly, continual monitoring of stream waters and sediments in Streets and Avondale Creek during and after the road upgrade is recommended. Monitoring of metal levels in stream sediments is important because these sediments are sinks for metals transported by stream waters.

7.4 Laboratory experiments

The use of adsorptive materials in a sand filter bed was suggested as a potential tertiary treatment option for the Kuranda Range Road Upgrade (Section 7.3.4.6). Hence, laboratory experiments were performed investigating the capacity of zeolite, mushroom compost and bentonite to sequester dissolved metals from road sediment leachates. These experiments were conducted over a 24 hour period and samples were collected at three intervals (5 minutes, 1 hour and 24 hours) to investigate the kinetic behaviour of the adsorptive materials. The experimental design was detailed in Chapter 2 – Section 2.8.1, while analytical techniques were discussed in Chapter 2 – Section 2.8.3.

7.4.1 Zeolite experiment

Control road sediment leachates and the leachates that were treated with the clinoptilolite zeolite were filtered (<0.45 μm) and analysed for their Cd, Cu, Pb, Ni and Zn concentrations. The data are shown in Table 7-10.

Metal values in the leachates treated with zeolite were similar to those concentrations in the control (untreated) waters (Table 7-10). Copper and Ni levels were only marginally lower in the treated solution compared with the untreated water (Table 7-10). By comparison, Pb concentrations were higher in the treated leachates than in the control samples collected at all three sampling junctures (Table 7-10). The Cd value in the treated leachate sample taken after 1 hour was higher than the Cd level in the corresponding untreated sample (Table 7-10). Only Zn concentrations were substantially lower in the zeolite-treated leachates than in the control solutions (Table 7-10).

Table 7-10: Metal values in control and zeolite-treated leachates. All concentrations are reported in µg/L.

	5 minutes		**1 hour**		**24 hours**	
	Control	*Treated*	*Control*	*Treated*	*Control*	*Treated*
Cd	0.40	0.32	0.512	1.02	0.436	0.331
Cu	99.9	96.2	124	115	73.9	64.9
Pb	18.6	20.7	17.4	21	19.1	27.8
Ni	21.9	20.7	28.9	25.1	23.4	21.9
Zn	2260	786	2830	1070	2370	377

The efficiency of the zeolite to remove metals from solution was calculated in the following manner:

$$\text{RE \%} = 100 - ([M]_T/[M]_C \times 100) \qquad \textbf{(Equation 7-1)}$$

where RE % is the removal efficiency expressed as a percentage, $[M]_T$ is the metal concentration in the treated solution and $[M]_C$ is the metal concentration in the control solution. The reliability of the removal efficiency values depends strongly on homogeneity (i.e. similar metal values) between the treated and control solutions; that is, it is assumed that the initial metal concentrations in the control and treatment solutions were similar to one another prior to the addition of the zeolite to the treatment solution. Homogeneity was verified by consistently similar metal values in parent and duplicate pond and leachate samples analysed throughout the research project (Appendix D).

Results in Table 7-11 show that the greatest removal efficiency value for Cd (25 %) from the zeolite-treated solution occurred 24 hours after the commencement of the experiment. Similarly, the highest removal efficiency for Cu (12 %) from the treated leachate was also recorded at the 24 hour juncture (Table 7-11). In contrast, the removal efficiencies for Pb in the treated solution continually decreased over the duration of the experiment (Table 7-11). In fact, negative removal efficiency values were documented for Pb in all samples (Table 7-11). Negative removal efficiency values reflect higher metal concentrations in the treated solutions than the untreated leachates. It is likely that Pb was released from the zeolite into the treatment solution, because similar trends were observed for solutions analysed at all three sample intervals (i.e. Pb values in the treated solutions were consistently higher than Pb values in the untreated waters).

The highest level of Ni reduction in the zeolite-treated water was observed in the sample collected after 1 hour (Table 7-11). By comparison, the zeolite was shown to reduce Zn concentrations in the solution by approximately 60 – 65 % after 5 minutes and 1 hour (Table 7-11). Following 24 hours, the Zn concentration in the treated solution was 82 % lower than the respective Zn value in the untreated water (Table 7-11).

Table 7-11: Metal removal efficiencies (%) for road sediment leachates treated with zeolite.

Sample collection time	**Cd**	**Cu**	**Pb**	**Ni**	**Zn**
5 minute	20	4	-10	5	65
1 hour	-50	7	-17	13	62
24 hour	25	12	-33	6	82

7.4.2 Mushroom compost experiment

Metal concentrations were analysed in leachate samples collected from the mushroom compost experiment and the data are shown in Table 7-12. The results of this experiment revealed that Cd, Cu, Pb and Zn concentrations were much lower in the leachates treated with compost than in the untreated leachates (Table 7-12).

This trend was evident for samples collected 5 minutes, 1 hour and 24 hours after the initiation of the laboratory experiment (Table 7-12).

Cadmium was below detection (0.05 μg/L) in all treated samples (Table 7-12). Copper concentrations were lowest in the treated sample collected upon 1 hour of settling with the compost (Table 7-12). By comparison, the treated leachate taken at the 24 hour-mark exhibited the lowest Pb and Zn concentrations (Table 7-12). Nickel values were below the detection limit (0.1 μg/L) in all treated and untreated samples (Table 7-12).

Table 7-12: Metal values in control and compost-treated leachates. All concentrations are reported in μg/L.

	5 minutes		**1 hour**		**24 hours**	
	Control	*Treated*	*Control*	*Treated*	*Control*	*Treated*
Cd	0.298	≤0.05	0.30	≤0.05	0.26	≤0.05
Cu	68.1	52	65.4	43	69.8	46.9
Pb	6.97	2.74	6.54	1.46	6.42	0.903
Ni	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1
Zn	2110	506	2090	307	2610	214

Removal efficiencies for metals in the compost-treated solution were calculated using Equation 7-1. Results in Table 7-13 show removal efficiencies of 81 % to 83 % for Cd in the treated solution for samples collected at all three junctures (Table 7-13). The highest removal efficiency value for Cu was observed in the treated leachates collected after 1 hour and 24 hours (Table 7-13). In comparison, the removal efficiency rates for Pb and Zn continuously increased over the course of the experiment (Table 7-13). Specifically, the Pb concentration in the compost-treated sample collected after 5 minutes was 61 % lower than the respective Pb level in the untreated sample and the removal efficiency rate for Pb in the treated sample taken after 24 hours was 86 % (Table 7-13). A similar pattern was observed for Zn concentrations (Table 7-13). The sample taken after 5 minutes revealed that 76 % of Zn was removed from the contaminated solution by the compost (Table 7-13). For the sample collected after 24 hours, the removal efficiency rate for Zn by the compost was 92 % (Table 7-13).

Table 7-13: Metal removal efficiencies (%) for road sediment leachates treated with compost.

Sample collection time	Cd	Cu	Pb	Ni	Zn
5 minute	83	23	61	0	76
1 hour	83	34	78	0	85
24 hour	81	33	86	0	92

7.4.3 Bentonite experiment

Data from the bentonite treatment experiment are presented in Table 7-14. As was the case with the results of the mushroom compost experiment, metal concentrations were generally much lower in the treated water samples than in the untreated leachates (Table 7-14). The exception to this was Cd in the samples collected after 5 minutes (Table 7-14). By comparison, Cu concentrations were lowest in the treated sample taken after 5 minutes of settling, while Pb, Ni and Zn values were all lowest in the sample taken 1 hour after the commencement of the experiment (Table 7-14). Results in Table 7-14 indicate an absence of sampling upon at the 24 hour-mark of the bentonite experiment. This is because at this particular juncture, the bentonite had formed a slurry with the water in the beaker, making it impossible to obtain a sample.

Table 7-14: Metal values in control and bentonite-treated leachates. All concentrations are reported in µg/L.

	5 minutes		**1 hour**	
	Control	*Treated*	*Control*	*Treated*
Cd	0.53	0.723	1.28	0.50
Cu	93.8	50.3	153	52.9
Pb	28.0	10.3	47.1	6.0
Ni	15.4	11.1	35.7	10.8
Zn	2750	202	4050	180

Removal efficiencies for metals in the bentonite-treated solution were also calculated using Equation 7-1. Results in Table 7-15 show a negative removal efficiency rate for Cd after 5 minutes (i.e. a higher Cd value was present in the treated solution than in the control leachate). However, after 1 hour, the removal efficiency rate for Cd was +61 % (Table 7-15).

Five minutes after the initiation of the experiment, the bentonite removed approximately 46 % of Cu from solution (Table 7-15). Moreover, after 1 hour, the removal efficiency rate for Cu increased to 65 % (Table 7-15). In comparison, the removal efficiency rate for Pb after 5 minutes was 63 % (Table 7-15). After 1 hour, however, 87 % of Pb in the contaminated solution was removed by the bentonite (Table 7-15).

The removal efficiency rates for Ni from the contaminated solution by the bentonite were 28 % and 60 % after 5 minutes and 1 hour, respectively (Table 7-15). The results of the experiment also revealed that Zn concentrations were 93 % and 96 % lower in the treated solution than the untreated water after 5 minutes and 1 hour, respectively (Table 7-15).

Table 7-15: Metal removal efficiencies (%) for road sediment leachates treated with bentonite.

Sample	**Cd**	**Cu**	**Pb**	**Ni**	**Zn**
5 minute	-33	46	63	28	93
1 hour	61	65	87	60	96

7.4.4 pH values and permeability measurements

The pH of the treated and control leachates was determined over the course of the remediation experiments and the data are presented in Table 7-16. The mixing of the road sediment with the distilled water increased the pH of the solution from 5.64 to near-neutral levels (Table 7-16). Moreover, the addition of zeolite to the road sediment leachates further increased the pH of the solutions (Table 7-16). In contrast, the compost and the bentonite reduced the pH of the contaminated water but not to levels below the near-neutral range (pH of 6 – 7) (Table 7-16).

Table 7-16: pH values of distilled water and control and treated leachates over various time intervals during the remediation experiments.

Sample collection time	**Distilled water**	**Control leachate**	**Zeolite leachate**	**Compost leachate**	**Bentonite leachate**
5 minute	5.64	6.67	6.88	6.49	6.23
1 hour	5.64	6.56	6.70	6.25	6.01
24 hour	5.64	6.94	7.05	6.38	6.12

The permeability of the materials used in the experiments was calculated by simple column-leach tests. The time taken for 200 mL of distilled water to pass through 50 g of each material was recorded and the results are given in Table 7-17.

The zeolite was the most permeable material used in the experiments, with unrestricted water flow observed through the zeolite layer in the column (Table 7-17). For the column containing the compost, water penetration through the layer was only slightly slower (Table 7-17). By comparison, the bentonite layer effectively plugged the column, and water was observed dripping from the column even after a period of 2 days (Table 7-17).

Table 7-17: Time taken for water to leach through columns containing 50 g of zeolite, compost and bentonite.

	Zeolite	**Compost**	**Bentonite**
Column leach times	5 seconds	15 seconds	2 days

7.5 Discussion

7.5.1 Summary of the properties of the adsorptive materials

Each of the studied materials possess strong adsorption capacities owing to their chemical properties (White 1997; Zhou et al. 2003). Zeolite, which is a group of aluminosilicate minerals, has a permanent net negative charge throughout its lattice structure (White 1997). Bentonite represents a group of swelling clay minerals including smectites (Ddani et al. 2005). There is a permanent net negative charge over the surface of the individual clay crystals (White 1997). Compost is generated by accelerating the rate of rate of humification of organic residues (White 1997). The adsorptive nature of compost stems from two of its main components: humic matter, which binds ionic metals from solution to form degradation-resistant organo-metallic compounds (Parker and Rae 1998); and microorganisms, which are able to sequester metals from solution (Bruins et al. 2000). The effectiveness of all of these materials in removing dissolved metals from road sediment leachates is discussed forthwith.

7.5.2 The adsorption experiments

The results of the remediation experiments indicated that heavy metal concentrations were generally lower in the waters that were treated with the various adsorptive materials than in the control (untreated) waters. This implies that the examined materials were capable of removing aqueous heavy metals from the road sediment leachates.

Removal capacity of the clinoptilolite zeolite

The clinoptilolite zeolite demonstrated high removal capacities for aqueous Zn in the road sediment leachates. However, the zeolite proved ineffective in lowering the aqueous levels of Cd, Cu, Pb and Ni. In fact, treatment of the contaminated waters with zeolite resulted in a corresponding increase in Pb in solution. This was particularly the case for samples collected 24 hours from the commencement of the experiment. It is possible that the solutions may not have had similar initial Pb values, resulting in greater Pb concentrations in the treated waters than the untreated solutions. However, this is unlikely for two reasons. Firstly, similar metal values were displayed between parent and duplicate pond and leachate solutions analysed throughout the study (Appendix D). Secondly, Pb values were higher in all three treated samples compared with the untreated waters, pointing towards the possible release of Pb from the zeolite.

The removal efficiency rates for the zeolite used in this study were compared with those determined for various remediation materials examined by other researchers (Table 7-18). Relatively low removal capacities were displayed by the zeolite assessed in this study in relation to the materials tested by other authors.

Table 7-18: Maximum removal rates (%) for heavy metals from urban stormwaters and simulated urban runoff waters in laboratory experiments. Where negative values are shown, metal values in the untreated solution were higher than in the control solution.

Author	***Treatment material/system used***	***Type of study***	***Cd***	***Cu***	***Pb***	***Ni***	***Zn***
This study	Zeolite (clinoptilolite) (24 hour)	Laboratory experiments examining road sediment leachates	25	12	-33	6	82
	Compost (24 hour)		81	33	86	0	92
	Bentonite (1 hour)		61	65	87	60	96
Pitcher et al. (2004)	Synthetic zeolite	Laboratory experiment examining spiked motorway stormwater	100	91.6	100	-	96.5
	Zeolites (mordenite)		6	32.4	44.2	-	10.1
Jang et al. (2005)	Hardwood bark mulch	Laboratory experiment involving synthetic solutions	-	80	90	-	80
Krikorian and Martin (2005)	Modified clay (kaolinite)	Laboratory experiment involving synthetic solutions	91	79	54	-	-
	Modified clay (montmorillonite)		93	85	-	31	-
Aldheimer and Bennerstedt (2003)	Sedimentation tank	Field study using road runoff waters	60	72	76	67	69
	Geotextile fabric		3-9	3-9	3-9	3-9	3-9
Zhou et al. (2003)	Peat filtration system	Field study using road runoff waters	-	-	-	-	83
Lau et al. (2000)	Biofilter	Field experiment using urban stormwater	-	90	-	-	90
Barrett et al. (1995)	Fine aggregate	Laboratory experiments	-	59	-	-	37
	Medium sand		-	13	-	-	59
	Gravel		-	-17	-	-	-6
	Compost		-	61	-	-	86
	Zeolites		-	39	-	-	70
	Grassy verge	Field study using road runoff waters	-	49	35	-	64

Previous studies have shown that zeolite demonstrates variable capacities to adsorb metals from contaminated solutions. For example, a study by Barrett et al. (1995) indicated that zeolite possesses limited capabilities to adsorb metals from contaminated solutions (Barrett et al. 1995). However, Um and Papelis (2005) demonstrated in a series of sorption experiments that clinoptilolite was able to sequester high levels of Pb from a contaminated solution. Moreover, the authors note that "the high affinity of Pb for clinoptilolite is well documented" (Um and Papelis 2004). Clearly, their results are discordant with those of this study; the adsorptive potential of the zeolite used in this study was extremely limited. It should be noted, however, that Um and Papelis's (2004) experiments involved the sorption of ionic Pb species, derived from the dissolution of readily soluble salts. In contrast, the Pb in the road sediment leachates examined in this study was likely present in a variety of phases, rather than simply ionic Pb species. Consequently, the results of this study are more likely to accurately reflect Pb sorption processes that could be expected to occur in road runoff waters.

The results given in Table 7-18 suggest that manufactured or synthetic zeolite displays a greater ability to remove metals from solution than naturally-occurring zeolite. For example, Pitcher et al. (2004) compared the capacities of a synthetic zeolite and a naturally-occurring zeolite (mordenite) to adsorb metals from stormwater runoff. The synthetic zeolite was able to sequester most of the metals in the captured runoff waters (Pitcher et al. 2004). However, the mordenite was less successful in metal attenuation. In fact, the clinoptilolite zeolite examined in this study demonstrated greater removal efficiencies for Cd and Zn from solution than the mordenite. Yet, the main problem with the use of synthetic zeolite as a remediation material is its high cost of production. Naturally-occurring zeolite minerals may be acquired at lower costs than manufactured materials (Payne and Abdel-Fattah 2004).

Removal capacity of the mushroom compost

The mushroom compost showed metal removal rates commensurate with removal efficiency values given by: a) modified clays (Krikorian and Martin 2005); naturally-occurring zeolite (Pitcher et al. 2004); b) mulch (Jang et al. 2005); a sediment holding tank (Aldheimer and Bennerstedt 2003); c) a peat filtration system (Zhou et al. 2003); a biofilter (Lau et al. 2000); and d) a range of sand and gravel materials (Barrett et al. 1995) (Table 7-18). In contrast to the results of the zeolite experiment, the mushroom compost demonstrated strong capabilities to sequester all of the analysed metals in the road sediment leachates (Table 7-18). This finding is important because no other studies have researched the ability of mushroom compost to remove metal contaminants from road sediment leachates or urban runoff waters. Mushroom compost is a commonly-available material that clearly displays remediation qualities.

Removal capacity of the bentonite clay

The bentonite displayed the greatest removal efficiency rates for Cu, Pb, Ni and Zn in the road sediment leachates in this study. Only for Cd was bentonite shown not to be the most efficient of the examined materials. Instead, the mushroom compost produced the highest removal rates for Cd. The data in Table 7-18 indicate that, generally, the studied bentonite clay has very high removal capabilities for all studied metals (Cd, Cu, Pb, Ni and Zn) compared with other materials investigated in previous studies.

Research conducted by Krikorian and Martin (2005) demonstrated that clays, modified with an ethanol-based catalyst and toluene, were able to sequester high amounts of metals that were present in solution as hydrolysed ions. These authors reported a much greater degree of success for the modified clay treatments than the corresponding unmodified clay treatments (Krikorian and Martin 2005). Their findings for the unmodified clays are in stark contrast to the results of this study, where bentonite clay granules in a completely unaltered form were shown to be capable of removing aqueous metals from solution. This is important because the use of materials with no pre-treatment in remediation systems has considerable economical advantages over the employment of modified materials (Pitcher et al. 2004).

Metal removal kinetics

The bentonite and the compost were extremely fast-acting in removing heavy metals from solution. Even after a period of only 5 minutes of interaction between these materials and the road sediment leachates, aqueous metal concentrations were much lower in the treated samples than in the untreated samples. The same was true for Zn levels in the zeolite-treated solution. This rapid rate of metal sequestration is an advantageous factor when considering potential applications for adsorptive materials to be included in roadside remediation structures. During the ‘wet season’ in tropical Australia, the ‘first flush’ waters are characterised by high metal loads (Chapter 4). It is this first delivery of waters that roadside remediation measures need to address. The results in this study indicated that compost and bentonite, and to a lesser extent zeolite, all have the potential to remove high concentrations of dissolved metals from metal-laden ‘first flush’ waters.

Implications of metal removal efficiencies

In summary, the remediation experiments conducted in this study have demonstrated that zeolite, bentonite and compost have the ability to remove aqueous metals from road sediment leachates. Further to results obtained by previous investigations, this study has shown that the studied materials are: a) effective in their non-modified forms; b) capable of removing the various forms of metals could be expected to occur in road runoff waters, rather than just removing ionic metal species derived from salts (e.g. metal acetates and nitrates) as has been documented in previous studies (e.g. Kriokorian and Martin 2005; Jang et al. 2005); and c) extremely fast-acting in lowering metal concentrations in road sediment leachates.

7.5.3 Significance of pH and permeability of adsorptive materials

Based on metal removal efficiencies alone, the materials assessed in this study show potential for their incorporation into roadside remediation systems. Nonetheless, their application depends on factors additional to their adsorptive capacities. Other chemical and physical properties, including pH and permeability, are important considerations in determining their potential to be used in remediation measures in roadside corridors. The importance of these parameters is discussed forthwith.

It has already been shown that road runoff waters commonly exhibit a near-neutral pH due to the buffering of slightly acidic rainwater by road sediments (Chapter 4). This near-neutral pH is a critical factor in limiting the solubility of heavy metals by inducing their adsorption onto solid phases (Rose et al. 2001). At pH values below 6, the adsorptive capacities of clay and oxide minerals diminish significantly (Parker and Rae 1998). It is therefore critical that any material used in remediation structures on road edges maintains a near-neutral pH within the treated road runoff waters. A study by Alvarez-Ayuso and Garcia-Sanchez (2003) documented the importance of a near-neutral soil pH in immobilising heavy metals. Their work examined the capacity of sepiolite, a type of clay, to immobilise soil Cd and Zn in a mined landscape in Spain. It was shown that decreases in soil pH below near-neutral levels (pH of approximately 6) significantly diminished the ability of the sepiolite to adsorb Cd and Zn (Alvarez-Ayuso and Garcia-Sanchez 2003). Similarly, a study in south Wales demonstrated that metal adsorption by clay soils is greatly reduced by pH decreases below near-neutral levels (Zuhairi 2003).

The peat filtration layer examined by Zhou et al. (2003) was found to decrease the pH of road runoff waters from 7.9 to 5.7 upon its discharge into the surrounding environment. Peat is characterised by acid pH values due to its high levels of humic and fulvic acids (White 1997). Thus, the effectiveness of the peat filtration layer was to some extent compromised by its acidity, which diminishes the capacity of the peat to adsorb metals.

Results of the experiments conducted in this study indicate that the three materials examined exerted minimal changes to the pH of the road sediment leachates (Table 7-16). The bentonite induced the greatest pH change in the contaminated solution, with a pH of 6.01 recorded in the treated sample collected after 1 hour. Nonetheless, the pH values for all treated waters examined in the experiments were in the near-neutral range (pH of 6 – 7). Therefore, use of these adsorptive materials in roadside remediation measures should not cause acid discharge. Furthermore, the adsorption capacities of the various materials examined in these experiments are optimal under such pH ranges. In their study examining mulches as adsorbers of heavy metals in contaminated solutions, Jang et al. (2005) noted that “it can be assumed that the H (hardwood bark) mulch with a neutral pH might exhibit better ability to hold cations than the other mulches with their lower pH”. Thus, pH is a critical factor controlling the adsorption of aqueous metals (Jang et al. 2005).

The permeability of the trialled materials is another important consideration for their application to treat road runoff waters. The respective permeabilities of the zeolite, compost and bentonite were assessed by simple flow tests. Results of these tests showed that the bentonite presented obvious permeability problems in treating flowing water. The column containing the bentonite effectively blocked water flow whereas the columns containing the zeolite and compost permitted minimal restrictions to flow through the columns (Table 7-17). The need for continual and uninhibited flow of runoff waters from road edges is an important consideration in designing any form of remediation structure. This is true of 'first flush' waters which transport the bulk proportion of contaminants from road surfaces (Glenn-III et al. 2001).

The obstacle of low permeability in allowing continual flow through the bentonite may be resolved at the design stage of the remediation structure. Some examples of design methods to overcome the low permeability of the bentonite are shown in Figure 7-6. The remediation systems depicted in the figure are rudimentary examples consisting of an open-ended container with a series of fining-down filtration layers.

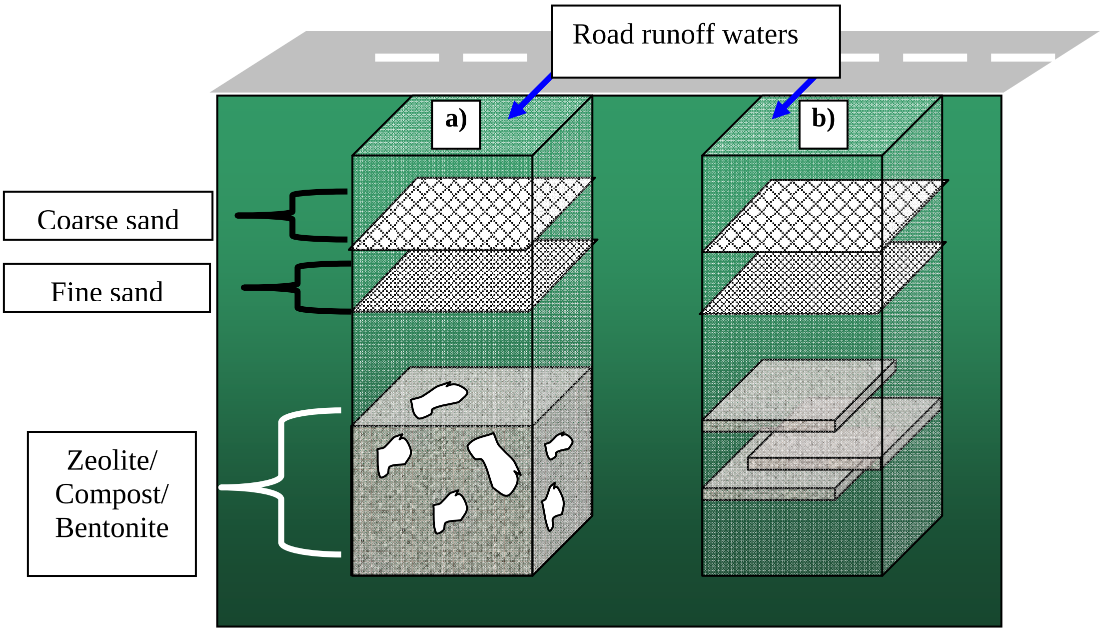

Figure 7-6: Filter remediation systems for the Kuranda Range Road Upgrade. The diagrams show designs to overcome low permeability of bentonite: a) incorporating porous material such as gravel to a zeolite/compost/bentonite layer; and b) staggering of unconnected zeolite/compost/bentonite layers.

The designs in Figure 7-6 show how the impermeable nature of bentonite can be overcome. Finally, zeolite, mushroom compost and bentonite may be incorporated into a pilot remediation structure, such as a filter unit, which is able to lower dissolved metal concentrations in road runoff waters.

7.5.4 Recommendations for future work

The laboratory experiments in this chapter focused on removal of aqueous (<0.45 μm diameter) heavy metals from road sediment leachates, which presumably exhibit a similar chemical composition to road runoff waters. The sequestration of metal phases associated with larger (>0.45 μm) suspended phases within road runoff waters is also important. Such metals may be released from their host particles into solution under slight changes in aqueous chemical conditions (Lee et al. 1997). Thus, further studies examining the efficiencies of adsorptive materials to remove aqueous metals from unfiltered waters are required. Moreover, the effectiveness of the adsorptive materials to treat other forms of dissolved contaminants (e.g. nutrients, pesticides) in road runoff waters needs to be researched.

7.6 Conclusions

Queensland Main Roads plan to upgrade the Kuranda Range Road from two lanes to four. Consequently, primary, secondary and tertiary treatment measures for road runoff waters discharged from the upgraded road will be required to negate the dispersal of pollutants into the adjoining World Heritage-listed landscape.

Queensland Main Roads have identified standing water bodies adjacent to the Kuranda Range Road as the most sensitive receptors to contaminated road runoff waters. Hence, remediation on the road upgrade is required at all points where the road will intersect the major catchments in the area. (i.e. streams that drain into Streets Creek and Avondale Creek). Bridges are planned for locations where the new road route traverses these creek crossings. Thus, treatment of road runoff waters from these bridges is necessary prior to their discharge into adjoining streams. The environmental sensitivity of the landscape surrounding the road precludes opportunities for the construction of water-holding treatment devices adjacent to the bridges. Hence, large-scale end-point and in-line pollutant traps such as trash rack weirs and constructed wetlands are not suited to the ecologically-sensitive landscape through which the Kuranda Range Road passes. Instead, smaller at-source pollutant traps (ASPTs) which can be emplaced into drainage culverts on the bridges of the upgraded road are viewed to be the most appropriate form of remediation for the Kuranda Range Road Upgrade.

The remediation measures proposed for the road upgrade in this study comprise a combination cost-effective primary, secondary and tertiary treatment technologies. Trash racks are viewed to be the most effective form of primary treatment, while filtration, adsorption and precipitation are seen to be the most suitable methods of secondary and tertiary treatment. All of these technologies have been demonstrated to be successful in treating road runoff waters in previous research.

Finally, the results of the laboratory experiments in this study demonstrated that bentonite and mushroom compost are able to sequester high levels of dissolved metals from road sediment leachates, even over a very short time (5 minutes). These materials have the potential to be incorporated into tertiary remediation measures, such as filter beds, specifically designed to treat road runoff waters.

Chapter 8 Summary and Conclusions

8.1 Summary of research

8.1.1 Revisiting the research question

The main objective pursued in this research project was to answer the question:

> *What are the key processes affecting the concentrations, mobility and bioavailability of traffic-derived metals in roadside environments in a section of the wet-dry tropics in northern Australia?*

The project thereby focused on the environmental distribution of five heavy metals: Cd, Cu, Pb, Ni and Zn; and to a lesser degree on Pd and Pt. These metals have been targeted in previous studies examining metal contamination within roadside environments (e.g. Sansalone and Buchberger 1997; Garcia and Millan 1998; Viklander 1998; Zereini and Alt 2000; and Zhou et al. 2003). The key findings and conclusions of the research are presented forthwith.

8.1.2 Metal accumulation in road sediments

Results of geochemical analyses performed on road sediments collected from the project area were discussed in Chapter 3. The analyses revealed the presence of various naturally-occurring (e.g. quartz) and anthropogenic (e.g. tyre rubber) particles. Furthermore, the road sediments exhibited variable total metal values including major concentrations of Zn (>1000 mg/kg), minor levels of Cu, Pb and Ni (ca. 10 to 1000 mg/kg) and trace amounts of Cd, Pd and Pt (<1 mg/kg). It was found that the road sediments were enriched in all metals (maximum enrichment factors: Cd 1.8x, Cu 1.5x, Pb 6.8x, Zn 17.3x, Pd 49.5x, Pt 82x), with the exception of Ni, relative to local background stream sediments. The magnified metal concentrations recorded in the road sediments were attributed to anthropogenic sources including abraded vehicle parts, vehicle emissions and road infrastructure and paving materials.

The results of this study demonstrated that metals were not necessarily restricted to the fine-grained (<75 µm) fraction of road sediments, as has been documented by previous studies (e.g. Viklander 1998; Varrica et al. 2003). For example, the 106 µm – 250 µm particle-size interval contained approximately 70 % of the total Zn content of the road sediments. Results from SEM/EDS observations and from Zn/C_{org} correlations confirmed that the amount of Zn in the road sediments depended primarily on the abundance of tyre rubber particles. Moreover, Ni displayed a bimodal distribution; the <38 µm fraction hosted approximately 40 % of the total Ni, whereas the >1000 µm interval accommodated ca. 15 % of the total Ni in the road sediments. The elevated Ni concentrations in the coarse sediments were attributed to the presence of Ni-rich basalt gravel, which is a common additive to road base (e.g. Van-Rooy 1991). In contrast, the primary sources of Ni in the fine-grained sediments are likely stainless steel shavings, presumably derived from engine and brake wear in motor vehicles (e.g. Varrica et al. 2003).

Results of a sequential extraction indicated that the bulk proportion (ca. 30 % to 95 %) of Cu, Pb, Ni and Zn hosted by the road sediments was present in acid-insoluble phases, likely residual silicate minerals. However, significant ($p<0.01$) positive correlations were observed between C_{org} and Cd, Cu, Pb and Zn concentrations in the road sediments. These correlations pointed to metal hosting by an organic source, most likely tyre rubber.

This project represents the first detailed examination of metal distributions in road sediments in wet-dry tropical locations. The data have shown that metal values may reach exceptionally high levels in such environments, particularly during the prolonged ‘dry season’. This was clearly demonstrated when comparing the results of this investigation with those of Diprose (1999). Heavy metal concentrations in road sediments collected from the Kuranda Range Road at the tail of the ‘wet season’ (April) by Diprose (1999) were much lower than their respective concentrations in the road sediments taken at the peak of the ‘dry season’ (July to November) in this study.

Moreover, the research revealed that common sequential and partial extractions utilised to infer metal hosting in soils and sediments are ineffective for road sediments. This is due to the resistant nature of tyre rubber particles under mildly acid reagents. The rubber shreds likely rapidly readsorb metals liberated into solution. Therefore, it is recommended that future studies of road sediments which employ partial or sequential extractions, should use complementary analyses such as C_{org} determinations and statistical processing of the geochemical data. The combination of such investigative tools will allow an understanding of the mobility, bioavailability and extractability of metals from road sediments.

8.1.3 Metal mobility in road runoff waters

Chapter 4 examined metal mobility in road runoff waters, road sediment leachates and road sediment ponded waters. The investigation revealed elevated Cu, Pb, and Zn concentrations (median values of 13.5 µg/L; 2.49 µg/L; and 235 µg/L, respectively) in filtered (<0.45 µm) road runoff waters collected from the Kuranda Range Road during an early 'wet season' rainfall event (in November 2004). Median Cu, Pb and Zn values in these filtered (<0.45 µm) road runoff waters were: 17x, 25x and 15x higher than their background levels. In comparison, Cu and Zn values in samples acquired during February 2003 and January 2004, after periods of heavy rainfall, were strongly diluted relative to the November 2004 samples. Despite this, median Cu, Pb and Zn concentrations in the road runoff waters sampled in February 2003 and January 2004 were still elevated (Cu 8x, Pb 27x and Zn 9x) above baseline levels (as determined by values in background stream samples).

The results from this study clearly indicated that runoff waters which flush over roads at the beginning of the 'wet season', remove the bulk proportion of metals from road surfaces. However, minor amounts of these metal contaminants remain on roads during the 'wet season'.

Column leach studies were performed on road sediments from the project area, and the results confirmed a 'first flush' pattern for Cd, Cu, Ni and Zn concentrations in the leachates. In contrast, only a weak 'first flush' effect was observed for Pb. Similar results have been noted in a previous study by Sansalone and Buchberger (1997), who examined the heavy metal concentrations in road runoff waters. Their study, however, was conducted in a wet temperate location in the USA where runoff events are more regularly-spaced annually (Sansalone and Buchberger 1997).

Ponding experiments conducted on the road sediments demonstrated a more gradual release of metals into solution than was documented in the column studies. Both the ponding and column experiments in this project revealed that less than 10 % of heavy metals within road sediments were mobilised as suspended phases (i.e. as determined by the unfiltered portion of the samples) and less than 5 % were water-soluble (i.e. as determined by the 0.45 µm filtrate).

Tyre rubber shreds in road sediments were observed to be an effective pH buffer. The presence of tyre rubber brought about a pH increase from approximately 5.7 to 7 in the distilled water used in the leaching and ponding experiments. This buffering capacity of the rubber particles has an important implication in limiting heavy metal mobility in road runoff waters. pH increases from slightly acid values to near-neutral levels have been reported to limit the solubility of heavy metals in road runoff waters, as metal adsorption onto suspended phases is favoured under near-neutral pH (Rose et al. 2001). Nonetheless, the link between pH buffering and tyre rubber has not been documented in other investigations of road runoff waters.

The dispersal of suspended and dissolved heavy metals by road runoff waters leads to their accumulation in roadside soils and water bodies. The advent of road runoff waters at the beginning of the 'wet season' in the tropics of Australia results in the mobilisation of exceptionally high concentrations of traffic-derived metals.

8.1.4 The dispersal of metals into streams intersected by roads

Metal distributions in stream sediments in the project area were discussed in Chapter 5. In that chapter it was shown that anthropogenic metals are sequestered by stream sediments in the Avondale Creek catchment, which receives road runoff waters from the Kuranda Range Road. Lead isotopic ratios and Pt concentrations revealed a subtle presence of anthropogenic contamination extending approximately

10 km from the rainforest headwaters on the Macalister Range to the mangrove estuary of the catchment system.

In the absence of other major anthropogenic metal repositories in the project area, roadside sources (i.e. motor vehicle, road infrastructure and road paving materials) were appointed as the principal cause of this contamination. Hence, the results of this study confirmed that Pb and Pt are efficient tracers of motor vehicle contamination. The dispersion of traffic-derived Pb and Pt over significant distances in stream systems may be facilitated by the elements' association with very fine-grained particles in roadside environments (e.g. Varrica et al. 2003).

This research represents the first investigation into the transport of traffic-derived metals to the fringe of the Great Barrier Reef. The anthropogenic metals detected in the estuary of the studied stream have the potential to be delivered to sediments within the Great Barrier Reef lagoon, particularly during flooding and cyclonic events.

8.1.5 The bioavailability of metals in roadside corridors

The bioavailability of metals in roadside soils and sediments was assessed in Chapter 6. Analyses of topsoils adjacent to the Kuranda Range Road revealed elevated Cd, Cu, Pb, Ni, Zn, Pd and Pt concentrations, above background values. Enrichment factors for metals in the roadside soils relative to the background substrates were Cd 2x, Cu, 10.5x, Pb 9x, Ni 8x, Zn 35x, Pd 3x and Pt 6x. Moreover, *M. repens* grasses growing in these roadside substrates displayed elevated stem tissue Zn values relative to background samples. Additionally, Cu, Pb, Ni and Zn concentrations were magnified in the root tissue of the roadside *M. repens* specimens compared to the background samples, indicating that heavy metals in topsoils adjacent to the Kuranda Range Road are bioavailable. These results were confirmed by a greenhouse experiment which demonstrated that heavy metals hosted by road sediments are bioavailable to *M. repens*.

DTPA-$CaCl_2$-TEA-HCl and EDTA-ammonium bicarbonate solutions were applied to road sediments and soils to determine metal bioavailability. The reagents proved to be rudimentary indicators of metal bioavailability in the roadside soils and the road sediments. However, strong differences in stem and root metal levels in the analysed grass species indicated that the bioavailability of contaminants is most accurately assessed by the analysis of organic tissue.

8.1.6 The remediation of road runoff waters

Remediation options for Kuranda Range Road Upgrade were discussed in Chapter 7. The selected ‘treatment train’ for the road involved primary, secondary and tertiary measures to remediate gross, suspended and dissolved pollutants from road runoff waters along the upgraded road. Consideration of the physical, ecological and climatic characteristics of the project area revealed that at-source pollutant attenuation is likely the most suitable form of treatment for the Kuranda Range Road Upgrade. Remediation of contaminated road runoff waters is most important at locations where the road will cross local streams (i.e. Streets Creek and Avondale Creek). Cost-effective technologies such as trash racks, sand and gravel filters and adsorption/biofiltration/precipitation basins have been demonstrated to be successful in remediating road runoff waters in previous studies. Together, these primary, secondary and tertiary treatment measures can be integrated into at-source pollutant traps which can be placed into drainage culverts on the upgraded Kuranda Range Road.

Finally, laboratory experiments were conducted to examine the effectiveness of zeolite, bentonite and mushroom compost to remove dissolved metals from road sediment leachates. The capacity of zeolite to capture dissolved metals in road runoff waters has been well-documented (e.g. Pitcher et al. 2004). However, no studies investigating the ability of bentonite and mushroom compost to sequester metals from road runoff waters or leachates have been performed. Results of the experiments revealed that the bentonite and compost demonstrated very high removal rates for Pb (87 %) and Zn (96 %) in the leachates, even over a very short time (5 minutes). The high metal removal rates exhibited by bentonite and compost highlight their potential to be applied to filter beds to treat road runoff waters.

8.1.7 Answering the research question

There are several key processes affecting the concentrations, mobility and bioavailability of traffic-derived metal contaminants in roadside environments in the wet-dry tropics in northern Australia. The prolonged ‘dry season’ results in metal accumulation in road sediments that settle on road surfaces. Metal values in road sediments may reach exceptionally high levels, especially in the absence of rainfall events. Hence, this study has shown that no simple positive relationship exists between road sediment metal values and traffic density in wet-dry tropical locations, which is contrary to findings for temperate locations (e.g. Schafer and Puchelt 1998). Instead, seasonal factors, such as drought and rainfall, cause temporal fluctuations in metal values on road surfaces in the wet-dry tropics.

At the end of the ‘dry season’, the most labile fractions of metals are mobilised from road surfaces by runoff waters during the relatively short ‘wet season’. This results in the delivery of traffic-derived metals to topsoils and streams that receive road runoff waters. As a result, roadside topsoils and stream sediments in wet-dry tropical regions may exhibit high metal values. The sequestration of metals by roadside topsoils and stream sediments may lead to their uptake by terrestrial and aquatic organisms. Metals incorporated into the tissue of these organisms are directed up local food-chains.

8.2 Implications of research

The rainforest adjacent to the Kuranda Range Road is listed as a World Heritage site and fulfils the criteria required for consideration as an area of Natural Heritage significance (UNESCO 2002). Hence, efforts should be made to mitigate negative environmental impacts adjacent to the Kuranda Range Road. However, results from this investigation revealed that elevated heavy metal levels in the soils adjacent to the road are accumulating in the tissue of a grass species (*M. repens*) growing along the road’s edge. The impacts of these contaminants on this particular grass species are of little consequence; *Melinis repens* is a declared weed in Australia. However, the fact that these traffic-derived metals were found to be bioavailable has implications. The occurrence of elevated metal concentrations in roadside soils can cause detrimental ecological impacts. The accumulation of heavy metals has been linked with reduced growth in roadside vegetation (Cook et al. 1994). Additionally, the presence of excessive heavy metal levels adjacent to roads can limit soil fertility, thus creating barren zones in roadside corridors (Zupancic 1999). Furthermore, even in cases where toxic effects are not observed in roadside vegetation, the presence of elevated soil-metal levels can result in changes in species composition (Forman and Alexander 1998). Any of these effects would be devastating for the vegetative communities adjacent to the Kuranda Range Road; a landscape renowned for its unique biodiversity.

The potential negative impacts of elevated soil-metal concentrations are not restricted to vegetation in roadside corridors. Anthropogenic metals, once incorporated into soils, have the potential to bioaccumulate up the trophic chain (Marino et al. 1992). For example, elevated Pb levels have been reported in the tissue of mammals living in close proximity to roads (Forman and Alexander 1998).

The delivery of traffic-derived metals from the surface of the Kuranda Range Road by road runoff waters represents another pathway by which these contaminants are able to ingress into the adjoining World Heritage-listed environment. Aquatic ecosystems are susceptible to heavy metal contaminants mobilised by road runoff waters (Sures et al. 2003). Moreover, fish mortalities within streams downgradient of roads have been related to high levels of Cu and Zn derived from roads (Forman and Alexander 1998).

An estimation of metal loadings determined in this study, reveals that metal build-up in local environments is a serious concern. This can be seen by examining the annual total metal loads discharged into roadside environments along the Kuranda Range Road. For example, assuming an average ‘first flush’ rainfall volume of 10000 L for each drainage point on the road, the total Zn loads mobilised during the ‘wet season’ may be calculated (Equation 8-1).

$$[\mathrm{Zn}]_F \times 10000\ \mathrm{L} = \mathrm{Zn}_{LD}\ (\mathrm{mg}) \qquad \textbf{(Equation 8-1)}$$

where, $[\mathrm{Zn}]_F$ is the ‘first flush’ Zn value (0.235 mg/L) and Zn_{LD} is the determined ‘first flush’ Zn load in mg. The ‘first flush’ Zn load for each drainage location can be calculated as:

0.235 x 10000 = 2350 mg or 2.35 kg.

Clearly, the cumulative loads of metals released into environments adjoining the Kuranda Range Road are very high.

The delivery of sediment-hosted metals in road runoff waters from the Kuranda Range Road has implications for another World Heritage-listed landscape: the Great Barrier Reef (GBR). This study confirmed the presence of traffic-derived metal contaminants within the estuary of a water catchment that feeds into the GBR. This finding raises the possibility that these metals are incorporated into reef lagoonal systems. To date, no studies have examined traffic-derived metal contamination in reef sediments. The potential negative effects of these contaminants entering the reef are therefore unknown. However, given the sensitivity of reef systems to changing chemical and physical conditions (Lough et al. 2002), it can only be concluded that the accumulation of metal contaminants in lagoonal sediments would be detrimental to the health of the reef ecosystem.

In summary, this research has demonstrated that two World Heritage environments are receptors of traffic-derived metal contaminants sourced from the Kuranda Range Road: the Wet Tropics World Heritage Area and the Great Barrier Reef World Heritage Area. The potential negative effects of these contaminants to the ecological health of these environments should not be underestimated, given prior documentation of adverse impacts by metals to roadside ecosystems (Cook et al. 1994; Forman and Alexander 1998). Traffic activities are on-going and hence, over time, there will be an ever-increasing load of metals entering roadside environments and receiving waters. Thus, the presence of these metal contaminants in roadside corridors adjacent to the Kuranda Range Road warrants an effort to limit their mobility. This may be achieved by mitigation at the point of delivery of the contaminants from the road’s edge (i.e. by remediation of road runoff waters that mobilise elevated metal loads during the ‘wet season’ in tropical Australia). Treatment of these waters will target the most labile and therefore most potentially bioavailable fraction of these contaminants.

8.3 Limitations and recommendations for future research

There are a number of limitations in the details and scope of this research. The principal limiting factor in the reliability of the data collected in this study centres on the extremely low concentrations of certain metals that were analysed. Cadmium, Pd and Pt presented the greatest problems relating to detection limits. Soil and sediment concentrations of these metals were commonly above the laboratory reported lower detection boundaries. However, for aqueous samples, Cd concentrations were frequently below the lower detection limits; particularly in the road runoff water samples. Palladium and Pt concentrations in aqueous samples consistently proved to be below the reach of the laboratory's lower detection limits.

The major limitation in the scope of the research was that it focused on the dispersal of traffic-derived metals only in ground level and below-ground media. The airborne dispersal of these contaminants has been documented to constitute an important dispersal pathway for traffic-derived metals, especially Pb and PGEs (Gulson et al. 1994a; Garty et al. 1996; Zereini and Alt 2000).

Furthermore, the fate of these metals in reef systems remains unexplored. Based on results of this study, an investigation of traffic-derived metal levels in lagoonal systems of the GBR should be pursued. Such a study could involve the analyses of reef lagoonal sediments for total heavy metal concentrations in association with Pb isotopic ratios, in order to discern a signature of anthropogenic contamination.

Another avenue of research that could be built upon from this study is an examination into the mobility and bioavailability of PGEs in roadside corridors in the wet-dry tropics of Australia. This work has demonstrated that Pd and Pt are present in elevated levels in road sediments and soils. However, there is no knowledge of the solubility and lability of these elements. An understanding of the behaviour of PGEs in roadside environments in wet-dry tropical regions would provide a useful contribution to the current sparse knowledge base on PGE contamination in roadside environments; which is based on studies conducted in temperate, northern hemisphere locations. Further to this, the distributions and concentrations of other metals and metalloids, such as As and Sb could be pursued in future roadside studies. Heavy traffic has been linked with high levels of dust Sb

(Thakur et al. 2004). It should be noted that Sb was analysed in a number of road sediment samples from this study; however, all Sb values were <5 mg/kg. Hence, no further research into this element was conducted in this particular investigation.

Additionally, future research may be conducted on the bioavailability of traffic-derived metals. This could include a study examining physiological factors influencing metal uptake by roadside grasses and plants. Such an investigation should focus on many different plant species as well as several individuals within the same species and assess the effects of various parameters (e.g. age, gender, species type) on metal bioavailability.

Finally, the construction and upgrade of any road must be accompanied by strategies to limit the dispersal of contaminants in road runoff waters. These strategies need to be based on accepted selection procedures and planning frameworks. Finalised treatment measures need to be specifically designed for individual roads. Furthermore, while various primary and secondary treatment technologies have been developed for contaminated road runoff waters, tertiary treatment devices are lacking. Only two commercially-available treatment devices for storm and road runoff waters currently exist: the StormFilter and the Electrocoagulation™ system. Clearly, there is the potential to develop existing adsorption, filtration and precipitation technologies into readily-available treatment devices specifically tailored for roadside environments.

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Appendix A – Sample ID and locations

Field samples

Sample type	Sample ID	Sample location	AMG coordinates	Sample date	Sample processing details	Analytical techniques	Analytes
Bedrock	B1 (Granite)	Macalister Range	CB585381	22.11.04	Crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	B2 (Sedimentary)	Macalister Range	CB584369	22.11.04	Crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	B3 (Hornfels)	Macalister Range	CB596376	22.11.04	Crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
Road sediments	KR1	Kuranda Range Road	CB599379	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR2	Kuranda Range Road	CB596372	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR3	Kuranda Range Road	CB601364	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR4	Kuranda Range Road	CB588370	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR5	Kuranda Range Road	CB587380	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR6	Kuranda Range Road	CB565391	23.10.02	Dried, sieved to less than 2mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	KR7	Kuranda Range Road	CB599379	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR8	Kuranda Range Road	CB596372	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR9	Kuranda Range Road	CB601364	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR10	Kuranda Range Road	CB588370	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR11	Kuranda Range Road	CB587380	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR12	Kuranda Range Road	CB565391	6.08.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR13	Kuranda Range Road	CB599379	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, Pd, Pt, C_{carb}, C_{org}
	KR14	Kuranda Range Road	CB596372	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR15	Kuranda Range Road	CB601364	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR16	Kuranda Range Road	CB588370	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR17	Kuranda Range Road	CB587380	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
					Dried, sieved to less than 75 µm	ICP-MS	$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (at CDU)
	KR18	Kuranda Range Road	CB565391	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR19	Kuranda Range Road	CB581386	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR20	Kuranda Range Road	CB599364	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR21	Kuranda Range Road	CB601379	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KR22	Kuranda Range Road	CB599379	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn

Field samples

Sample type	Sample ID	Sample location	AMG coordinates	Sample date	Sample processing details	Analytical techniques	Analytes
Road sediment	KR23	Kuranda Range Road	CB596372	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR24	Kuranda Range Road	CB601364	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR25	Kuranda Range Road	CB588370	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR26	Kuranda Range Road	CB587380	27.08.04	Dried, sieved to less than 2mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR27	Kuranda Range Road	CB565391	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR28	Kuranda Range Road	CB581386	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR29	Kuranda Range Road	CB599364	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR30	Kuranda Range Road	CB601379	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 μm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	CR1	Captain Cook Hwy, roundabout	CB606399	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR2	Captain Cook Hwy, roundabout	CB606375	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR3	Captain Cook Hwy, roundabout	CB611368	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR4	Captain Cook Hwy, roundabout	CB647350	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/XRF	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
					Dried, sieved to less than 75 μm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	CR5	Captain Cook Hwy	CB599420	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR6	Captain Cook Hwy	CB598421	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR7	Captain Cook Hwy	CB598422	23.10.02	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO
	CR8	Captain Cook Hwy, roundabout	CB606399	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	CR9	Captain Cook Hwy, roundabout	CB606375	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, Pd, Pt, C_{carb}, C_{org}
					Dried, sieved to less than 75 μm	ICP-MS	^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	CR10	Captain Cook Hwy, roundabout	CB611368	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	CR11	Captain Cook Hwy, roundabout	CB647350	12.11.03	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	CR12	Captain Cook Hwy, roundabout	CB606399	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR13	Captain Cook Hwy, roundabout	CB606375	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR14	Captain Cook Hwy, roundabout	CB611368	27.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Stream sediment	S1	Streets Creek	CB565392	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill.	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	S2	Streets Creek	CB566392	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S3	Streets Creek	CB567392	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt

Field samples

Sample type	**Sample ID**	**Sample location**	**AMG coordinates**	**Sample date**	**Sample processing details**	**Analytical techniques**	**Analytes**
Stream sediment	S4	Streets Creek	CB568392	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S5	Streets Creek	CB569394	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	S6	Streets Creek	CB569395	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S7	Streets Creek	CB571395	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	S8	Streets Creek	CB571396	27.02.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S9	Avondale Creek	CB583366	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill. Sieved in Malvern Mastersizer Laser Particle Size Analyser	ICP-AES/ICP-MS/XRF/NDIR/gravimetric precip.	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO, C_{org}, $S_{sulfate}$, $S_{sulfide}$, S
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S10	Avondale Creek	CB583367	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S11	Avondale Creek	CB584367	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S12	Avondale Creek	CB584368	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S13	Avondale Creek	CB585368	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S14	Avondale Creek	CB585369	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S15	Avondale Creek	CB593373	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S16	Avondale Creek	CB595375	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S17	Avondale Creek	CB600376	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)
	S18	Avondale Creek	CB607374	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S19	Avondale Creek	CB610371	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb (at CDU) and ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb (at ANSTO)

Field samples

Sample type	Sample ID	Sample location	AMG coordinates	Sample date	Sample processing details	Analytical techniques	Analytes
Stream sediment	S20	Avondale Creek	CB611371	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill.	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt,
					Dried, sieved to less than 75 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	S21	Avondale Creek	CB612372	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill. Sieved in Malvern Mastersizer Laser Particle Size Analyser	ICP-AES/ICP-MS/XRF/NDIR/gravimetric precip.	Al_2O_3, Fe_2O_3, MnO, C_{org}, $S_{sulfate}$, $S_{sulfide}$, S
					Dried, sieved to less than 75 µm	ICP-MS	$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (at CDU) and $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ (at ANSTO)
	S22	Avondale Creek	CB614375	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (at CDU) and $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ (at ANSTO)
	S23	Avondale Creek	CB632389	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
					Dried, sieved to less than 75 µm	ICP-MS	$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (at CDU) and $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ (at ANSTO)
	S24	Avondale Creek	CB648400	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
					Dried, sieved to less than 75 µm	ICP-MS	Pb isotopic ratios
	S25	Avondale Creek	CB649399	14.10.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill. Sieved in Malvern Mastersizer Laser Particle Size Analyser	ICP-AES/ICP-MS/XRF/NDIR/gravimetric precip.	Cd, Cu, Pb, Ni, Zn, Pd, Pt, Al_2O_3, Fe_2O_3, MnO, C_{org}, $S_{sulfate}$, $S_{sulfide}$, S
					Dried, sieved to less than 75 µm	ICP-MS	$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (at CDU) and $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ (at ANSTO)
Road runoff waters	KW1	Kuranda Range Road	CB599379	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KW2	Kuranda Range Road	CB596372	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KW3	Kuranda Range Road	CB601364	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KW4	Kuranda Range Road	CB588370	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KW5	Kuranda Range Road	CB581386	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KW6	Kuranda Range Road	CB599379	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW7	Kuranda Range Road	CB601364	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW8	Kuranda Range Road	CB587380	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW9	Kuranda Range Road	CB581386	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW10	Kuranda Range Road	CB599379	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW11	Kuranda Range Road	CB596372	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW12	Kuranda Range Road	CB601364	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW13	Kuranda Range Road	CB588370	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC

Field samples

Sample type	Sample ID	Sample location	AMG coordinates	Sample date	Sample processing details	Analytical techniques	Analytes
Road runoff waters	KW14	Kuranda Range Road	CB587380	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW15	Kuranda Range Road	CB565391	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW16	Kuranda Range Road	CB581386	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW17	Kuranda Range Road	CB599364	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	KW18	Kuranda Range Road	CB601379	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW1	Captain Cook Hwy, roundabout	CB606399	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	CW2	Captain Cook Hwy, roundabout	CB606375	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	CW3	Captain Cook Hwy, roundabout	CB611368	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	CW4	Captain Cook Hwy, roundabout	CB647350	5.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	CW5	Captain Cook Hwy, roundabout	CB606399	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW6	Captain Cook Hwy, roundabout	CB606375	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW7	Captain Cook Hwy, roundabout	CB611368	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW8	Captain Cook Hwy, roundabout	CB647350	23.01.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW9	Captain Cook Hwy, roundabout	CB606399	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW10	Captain Cook Hwy, roundabout	CB606375	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW11	Captain Cook Hwy, roundabout	CB611368	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
	CW12	Captain Cook Hwy, roundabout	CB647350	14.11.04	Split into 2 subsamples, filtered (0.45 µm) and unfiltered	ICP-MS/pH and EC recording instruments	Cd, Cu, Pb, Ni, Zn, pH, EC
Stream waters	S_W1	Streets Creek	CB565392	27.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
	S_W2	Streets Creek	CB571396	27.02.03	Filtered (0.45 µm)	ICP-MS	Cd, Cu, Pb, Ni, Zn
Rainwater	R_W1	Yorkeys Knob	CB641410	29.11.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W2	Yorkeys Knob	CB641410	29.11.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W3	Yorkeys Knob	CB641410	31.11.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W4	Yorkeys Knob	CB641410	31.11.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W5	Yorkeys Knob	CB641410	31.11.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W6	Yorkeys Knob	CB641410	1.12.04	Unfiltered	pH,EC recording instruments	pH, EC
	R_W7	Yorkeys Knob	CB641410	1.12.04	Unfiltered	pH,EC recording instruments	pH, EC
Grasses	KG1-i	Kuranda Range Road	CB599379	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG2	Kuranda Range Road	CB593374	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn

Field samples

Sample type	Sample ID	Sample location	AMG coordinates	Sample date	Sample processing details	Analytical techniques	Analytes
Grasses	KG3-i	Kuranda Range Road	CB596372	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG4-i	Kuranda Range Road	CB598366	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG5	Kuranda Range Road	CB601364	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG6	Kuranda Range Road	CB596365	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG7-i	Kuranda Range Road	CB587380	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG1-ii	Kuranda Range Road	CB599379	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG3-ii	Kuranda Range Road	CB596372	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG4-ii	Kuranda Range Road	CB598366	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	KG7-ii	Kuranda Range Road	CB587380	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	DG1	Field off Davies Ck Road	CB475205	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	DG2	Field off Davies Ck Road	CB477205	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	DG3	Field off Davies Ck Road	CB476204	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	DG4	Field off Davies Ck Road	CB475203	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
	DG5	Field off Davies Ck Road	CB477203	9.08.04	Washed, dried, weighed, ashed, acid digest	ICP-MS	Cd, Cu, Pb, Ni, Zn
Topsoils	KT1-i	Kuranda Range Road	CB599379	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT2	Kuranda Range Road	CB593374	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT3-i	Kuranda Range Road	CB596372	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT4-i	Kuranda Range Road	CB598366	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT5	Kuranda Range Road	CB601364	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT6	Kuranda Range Road	CB596365	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT7-i	Kuranda Range Road	CB587380	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT1-ii	Kuranda Range Road	CB599379	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT3-ii	Kuranda Range Road	CB596372	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT4-ii	Kuranda Range Road	CB598366	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	KT7-ii	Kuranda Range Road	CB587380	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	DT1	Field off Davies Ck Road	CB475205	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	DT2	Field off Davies Ck Road	CB477205	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	DT3	Field off Davies Ck Road	CB476204	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	DT4	Field off Davies Ck Road	CB475203	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt
	DT5	Field off Davies Ck Road	CB477203	9.08.04	Dried, sieved to less than 2 mm, crushed to powder in chrome steel ring mill	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn, Pd, Pt

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Supernatant	L1	Sequential extraction (water-soluble step)	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L2	Sequential extraction (exchangeable step)	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L3	Sequential extraction (carbonate step)	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L4	Sequential extraction (oxide/oxyhydroxide step)	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L5	Sequential extraction (organic/sulphide step)	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L6a	Citrate dithionite partial extraction – Kuranda Range Road sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L6b	Citrate dithionite partial extraction – Kuranda Range Road sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L6c	Citrate dithionite partial extraction – Kuranda Range Road sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L6d	Citrate dithionite partial extraction – Kuranda Range Road sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L7a	Citrate dithionite partial extraction – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L7b	Citrate dithionite partial extraction – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L7c	Citrate dithionite partial extraction – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L7d	Citrate dithionite partial extraction – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	17.07.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L8a	DTPA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L8b	DTPA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L8c	DTPA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L8d	DTPA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L9a	DTPA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L9b	DTPA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Supernatant	L9c	DTPA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L9d	DTPA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L10a	EDTA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L10b	EDTA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L10c	EDTA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L10d	EDTA Bioavailable extractions – Kuranda Range Road sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L11a	EDTA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L11b	EDTA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L11c	EDTA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L11d	EDTA Bioavailable extractions – Captain Cook Highway roundabout sediments	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L12	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT1-i)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L13	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT1-ii)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L14	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT2)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L15	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT3-i)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L16	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT3-ii)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L17	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT4-i)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L18	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT4-ii)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Supernatant	L19	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT5)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L20	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT6)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L21	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT7-i)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L22	DTPA Bioavailable extractions – Kuranda Range Road topsoils (KT7-ii)	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L23	DTPA Bioavailable extractions – Davies Creek Road topsoils	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L24	DTPA Bioavailable extractions – Davies Creek Road topsoils	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L25	DTPA Bioavailable extractions – Davies Creek Road topsoils	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L26	DTPA Bioavailable extractions – Davies Creek Road topsoils	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Supernatant	L27	DTPA Bioavailable extractions – Davies Creek Road topsoils	As per procedure in Appendix C	13.08.04	As per procedure in Appendix C	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Leachate (distilled water)	L28	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L29	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L30	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L31	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L32	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L33	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L34	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L35	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Leachate (distilled water)	L36	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L37	Column leach experiment – Kuranda Range Road sediments	Immediate	18.05.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L38	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L39	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L40	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L41	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L42	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L43	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L44	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L45	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L46	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Leachate (distilled water)	L47	Column leach experiment – Captain Cook Highway roundabout sediments	Immediate	1.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L48	Ponding experiment – Kuranda Range Road sediments	5 minutes	23.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L49	Ponding experiment – Kuranda Range Road sediments	1 hour	23.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L50	Ponding experiment – Kuranda Range Road sediments	24 hours	24.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L51	Ponding experiment – Kuranda Range Road sediments	1 week	30.06.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L52	Ponding experiment – Kuranda Range Road sediments	1 month	21.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Pond decant (distilled water)	L53	Ponding experiment - Captain Cook Highway roundabout sediments	5 minutes	4.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L54	Ponding experiment - Captain Cook Highway roundabout sediments	1 hour	4.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L55	Ponding experiment - Captain Cook Highway roundabout sediments	24 hours	5.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L56	Ponding experiment - Captain Cook Highway roundabout sediments	48 hours	6.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L57	Ponding experiment - Captain Cook Highway roundabout sediments	1 week	11.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L58	Ponding experiment - Captain Cook Highway roundabout sediments	2 week	18.07.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L59	Ponding experiment - Captain Cook Highway roundabout sediments	5 weeks	8.08.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L60	Ponding experiment - Captain Cook Highway roundabout sediments	6 weeks	15.08.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Pond decant (distilled water)	L61	Ponding experiment - Captain Cook Highway roundabout sediments	3 months	4.10.03	Split into 2 subsamples: filtered (0.45 μm) and unfiltered. Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh, DO recording instruments	Cd, Cu, Pb, Ni, Zn, Al, Fe, Ca, pH, Eh, DO
Decant (distilled water)	L62	Car tyre ponding experiment	5 minutes	17.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L63	Car tyre ponding experiment	1 hour	17.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L64	Car tyre ponding experiment	24 hours	18.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L65	Car tyre ponding experiment	1 week	25.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 %HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L66	Car tyre ponding experiment	1 month	16.12.04	Filtered (0.45 μm). Acidified with 2 drops of 70 %HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L67	Truck tyre ponding experiment	5 minutes	17.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 %HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L68	Truck tyre ponding experiment	1 hour	17.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 %HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L69	Truck tyre ponding experiment	24 hours	18.11.04	Filtered (0.45 μm). Acidified with 2 drops of 70 %HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Decant (distilled water)	L70	Truck tyre ponding experiment	1 week	25.11.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Decant (distilled water)	L71	Truck tyre ponding experiment	1 month	16.12.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH, Eh recording instruments	Cd, Cu, Pb, Ni, Zn, pH, Eh
Potted grass	L72	Greenhouse experiment – Kuranda Range Road sediments	15 weeks	21.2.05	Washed, dried, weighed, ashed, acid digest	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Potted grass	L73	Greenhouse experiment – Kuranda Range Road sediments	15 weeks	21.2.05	Washed, dried, weighed, ashed, acid digest	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Potted grass	L74	Greenhouse experiment – Captain Cook Highway roundabout sediments	15 weeks	21.2.05	Washed, dried, weighed, ashed, acid digest	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Pond decant (distilled water)	L75	Zeolite remediation experiment – control	5 minutes	20.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L76	Zeolite remediation experiment – test	5 minutes	20.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L77	Zeolite remediation experiment – control	1 hour	20.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L78	Zeolite remediation experiment – test	1 hour	20.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L79	Zeolite remediation experiment – control	24 hours	21.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L80	Zeolite remediation experiment – test	24 hours	21.03.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L81	Mushroom compost remediation experiment – control	5 minutes	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L82	Mushroom compost remediation experiment – test	5 minutes	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L83	Mushroom compost remediation experiment – control	1 hour	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L84	Mushroom compost remediation experiment – test	1 hour	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L85	Mushroom compost remediation experiment – test	24 hours	10.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO_3	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH

Laboratory experiment samples

Sample type	Sample ID	Experiment	Collection time (from commencement of experiment)	Sample date	Sample processing details	Analytical techniques	Analytes
Pond decant (distilled water)	L86	Mushroom compost remediation experiment – test	24 hours	10.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO$_3$	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L87	Bentonite remediation experiment – control	5 minutes	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO$_3$	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L88	Bentonite remediation experiment – test	5 minutes	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO$_3$	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L89	Bentonite remediation experiment – control	1 hour	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO$_3$	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH
Pond decant (distilled water)	L90	Bentonite remediation experiment – test	1 hour	9.08.04	Filtered (0.45 µm). Acidified with 2 drops of 70 % HNO$_3$	ICP-AES/ICP-MS/pH recording instrument	Cd, Cu, Pb, Ni, Zn, pH

Sieved and composite sediment samples

Sample type	Sample ID	Sample source	Sample date	Sieve fraction	Analytical techniques	Analytes
Road sediment (bulk composite sample)	KRC$_M$1		23.10.02		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CRC$_M$1		23.10.02		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KRC$_M$2		12.11.03		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CRC$_M$2		12.11.03		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KRC$_M$3		27.08.04		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CRC$_M$3		27.08.04		ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
Road sediment (sieve fraction)	KR$_F$1	KRC$_M$1	23.10.02	<38 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$2	KRC$_M$1	23.10.02	38 µm - 63 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$3	KRC$_M$1	23.10.02	63 µm - 75 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$4	KRC$_M$1	23.10.02	75 µm - 106 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$5	KRC$_M$1	23.10.02	106 µm - 250 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$6	KRC$_M$1	23.10.02	250 µm - 500 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$7	KRC$_M$1	23.10.02	500 µm - 1 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$8	KRC$_M$1	23.10.02	1mm - 2 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_F$9	KRC$_M$1	23.10.02	2 mm - 4 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn

Sieved and composite sediment samples

Sample type	**Sample ID**	**Sample source**	**Sample date**	**Sieve fraction**	**Analytical techniques**	**Analytes**
Road sediment (sieve fraction)	KR$_{F}$10	KRC$_{M}$1	23.10.02	>4 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$1	CRC$_{M}$1	23.10.02	<38 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	KR$_{F}$11	KRC$_{M}$2	12.11.03	<38 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	KR$_{F}$12	KRC$_{M}$2	12.11.03	63 µm - 75 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	KR$_{F}$13	KRC$_{M}$2	12.11.03	106 µm - 250 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	KR$_{F}$14	KRC$_{M}$2	12.11.03	500 µm - 1 mm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	KR$_{F}$15	KRC$_{M}$2	12.11.03	2 mm - 4 mm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	KR$_{F}$16	KRC$_{M}$3	27.08.04	<38 µm	ICP-MS	Pd, Pt
	KR$_{F}$17	KRC$_{M}$3	27.08.04	38 µm - 75 µm	ICP-MS/NDIR	Pd, Pt, C$_{org}$
	KR$_{F}$18	KRC$_{M}$3	27.08.04	75 µm - 250 µm	ICP-MS/NDIR	Pd, Pt, C$_{org}$
	KR$_{F}$19	KRC$_{M}$3	27.08.04	250 µm - 2 mm	ICP-MS	Pd, Pt
	CR$_{F}$2	CRC$_{M}$1	23.10.02	38 µm - 63 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$3	CRC$_{M}$1	23.10.02	63 µm - 75 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$4	CRC$_{M}$1	23.10.02	75 µm - 106 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$5	CRC$_{M}$1	23.10.02	106 µm - 250 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$6	CRC$_{M}$1	23.10.02	250 µm - 500 µm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$7	CRC$_{M}$1	23.10.02	500 µm - 1 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$8	CRC$_{M}$1	23.10.02	1mm - 2 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$9	CRC$_{M}$1	23.10.02	2 mm - 4 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$10	CRC$_{M}$1	23.10.02	>4 mm	ICP-AES/ICP-MS	Cd, Cu, Pb, Ni, Zn
	CR$_{F}$11	CRC$_{M}$2	12.11.03	<38 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	CR$_{F}$12	CRC$_{M}$2	12.11.03	63 µm - 75 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	CR$_{F}$13	CRC$_{M}$2	12.11.03	106 µm - 250 µm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	CR$_{F}$14	CRC$_{M}$2	12.11.03	500 µm - 1 mm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	CR$_{F}$15	CRC$_{M}$2	12.11.03	2 mm - 4 mm	ICP-AES/ICP-MS/NDIR	Cd, Cu, Pb, Ni, Zn, C$_{org}$
	CR$_{F}$16	CRC$_{M}$3	27.08.04	<38 µm	ICP-MS	Pd, Pt
	CR$_{F}$17	CRC$_{M}$3	27.08.04	38 µm - 75 µm	ICP-MS/NDIR	Pd, Pt, C$_{org}$
	CR$_{F}$18	CRC$_{M}$3	27.08.04	75 µm - 250 µm	ICP-MS/NDIR	Pd, Pt, C$_{org}$
	CR$_{F}$19	CRC$_{M}$3	27.08.04	250 µm - 2 mm	ICP-MS/NDIR	Pd, Pt, C$_{org}$

Appendix B – Sample data spreadsheet

Bedrock samples

	Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**
Laboratory	ALS	ALS	ALS	ALS	ALS	ALS	ALS
Sample ID							
B1 (Granite)	0.03	26.8	19	18	79	0.008	0.0067
B2 (Sedimentary)	0.04	66.5	20.1	20.5	86	0.003	0.0023
B3 (Hornfels)	0.02	18.6	8.9	16.8	74	0.003	0.0026

Road sediment samples

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**	**Al_2O_3 (wt %)**	**Fe_2O_3 (wt %)**	**MnO (wt %)**	**C_{org} (wt %)**	**C_{carb} (wt %)**	**^{208}Pb/ ^{206}Pb**	**^{207}Pb/ ^{206}Pb**	**Total Pb (mg/kg)**
	Laboratory	ALS	ALS	ALS	ALS	ALS	ALS	ALS	AAC	AAC	AAC	ALS	ALS	CDU	CDU	CDU
Sample ID	***Sieve fraction***															
KR1	<2 mm	0.19	34	123	36	1100	0.246	0.438	5.05	3.88	0.05					
KR2	<2 mm	0.29	44	53.7	94	2200	0.102	0.314	7.25	5.41	0.10					
KR3	<2 mm	0.13	66	174	29	235	0.093	0.355	6.12	3.73	0.07					
KR4	<2 mm	0.08	32	55	38	357	0.02	0.0382	10.3	5.04	0.08					
KR5	<2 mm	0.14	31	29.3	60	804	0.073	0.0908	8.78	5.62	0.07					
KR6	<2 mm	0.19	60	43.9	75	966	0.269	0.155	9.32	7.45	0.13					
KR7	<2 mm	0.05	19.2	53.5	34	112	0.003	0.0041								
KR8	<2 mm	0.21	40.8	147	43.9	1150	0.029	0.163								
KR9	<2 mm	0.15	33.1	161	42.2	900	0.039	0.354								
KR10	<2 mm	0.20	43	11.8	47.6	1030	0.03	0.0522								
KR11	<2 mm	0.25	42.1	34.6	47.7	451	0.104	0.0969								
KR12	<2 mm	0.25	71	39.6	28.7	1050	0.25	0.329								
KR13	<2 mm	0.26	49.6	21.1	41.2	1160	0.013	0.0269				9.5	3			
KR14	<2 mm	0.25	46.4	53	29.6	2070	0.105	0.0417								
KR15	<2 mm	0.14	49.5	36.5	43.9	174	0.04	0.0258								
KR16	<2 mm	0.18	19.4	55.4	44.1	268	0.001	0.0021								
KR17	<2 mm	0.24	44.9	422	51	1410	0.023	0.04								
	<75 µm													2.097	0.869	448
KR18	<2 mm	0.12	32.9	110	36.4	647	0.053	0.0813								
KR19	<2 mm	0.36	52.1	25.2	35.3	2790	0.014	0.0269								
KR20	<2 mm	0.44	43.8	103	26.3	2780	0.114	0.162								

Sample ID	*Sieve fraction*	**Cd (mg/kg)**	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**	**Al_2O_3 (wt %)**	**Fe_2O_3 (wt %)**	**MnO (wt %)**	**C_{org} (wt %)**	**C_{carb} (wt %)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**$^{208}Pb/^{204}Pb$**	**$^{206}Pb/^{204}Pb$**	**Total Pb (mg/kg)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**Total Pb (mg/kg)**
	Laboratory	ALS	ALS	ALS	ALS	ALS	ALS	ALS	AAC	AAC	AAC	ALS	ALS	ANSTO	ANSTO	ANSTO	ANSTO	ANSTO	CDU	CDU	CDU
KR21	<2 mm	0.16	55.4	165	40	201	0.027	0.0453													
KR22	<2 mm	0.31	41.3	24.8	39.5	2810	0.023	0.355													
KR23	<2 mm	0.35	179	35.1	31.9	3320	0.021	0.0517													
KR24	<2 mm	0.13	46.9	35.3	68.1	322															
KR25	<2 mm	0.09	27.4	12	42.3	346															
KR26	<2 mm	0.30	31.6	31.5	26.7	2170															
KR27	<2 mm	0.12	26.5	20.1	24.5	686															
KR28	<2 mm	0.18	31.8	225	38	780	0.021	0.189													
KR29	<2 mm	0.09	40.4	232	35.3	274															
KR30	<2 mm	0.18	33.4	73.1	26	557															
	<75 µm													2.0892	0.9162	34.6143	16.5679	50.9	2.126	0.881	64.2
CR1	<2 mm	0.10	37	117	34	548	0.359	0.573	5.35	3.60	≤0.05										
CR2	<2 mm	0.19	52	168	37	895	0.706	1.050	5.17	4.13	≤0.05										
CR3	<2 mm	0.19	48	115	34	619	0.923	0.664	4.91	3.77	≤0.05										
CR4	<2 mm	0.24	33	196	30	619	0.245	0.507	5.06	2.93	≤0.05										
	<75 µm													2.1112	0.9377	34.5659	16.3728	157	2.132	0.894	272
CR5	<2 mm	0.16	21	61.9	25	387	0.055	0.0576	10.2	3.75	0.06										
CR6	<2 mm	0.15	36	96.4	65	436	0.111	0.1120	7.79	4.52	0.06										
CR7	<2 mm	0.21	36	976	28	1040	0.043	0.0559	6.31	3.51	0.06										
CR8	<2 mm	0.22	72.1	105	31.2	632	0.099	0.1540													
CR9	<2 mm	0.30	121	150	32.3	1000	0.112	0.151				3.4	0.9								
	<75 µm													2.10617	0.9322	34.5760	16.4166	133			
CR10	<2 mm	0.21	57.4	214	37.5	710	0.075	0.0797													
CR11	<2 mm	0.23	72.8	100	30.2	596	0.077	0.183													
CR12	<2 mm	0.11	32	44.3	29.6	377	0.047	0.0839													
CR13	<2 mm	0.15	89.1	74.7	38.2	795	0.043	0.0664													
CR14	<2 mm	1.22	61.6	44.4	40.4	489	0.079	0.1350													

Stream sediment samples

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**	**Al_2O_3 (mg/kg)**	**Fe_2O_3 (mg/kg)**	**MnO (mg/kg)**	**C_{org} (wt %)**	**S (wt %)**	**$S_{sulfate}$ (wt %)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**$^{208}Pb/^{204}Pb$**	**$^{206}Pb/^{204}Pb$**	**Total Pb (mg/kg)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**Total Pb (mg/kg)**
	Laboratory	ALS	ALS	ALS	ALS	ALS	ALS	ALS	AAC	AAC	AAC	ALS	ALS	ALS	ANSTO	ANSTO	ANSTO	ANSTO	ANSTO	CDU	CDU	CDU
Sample ID	***Sieve fraction***																					
S1	<2 mm	0.03	27.5	20.7	15.4	20	0.001	0.0006				1.18										
S2	<2 mm	0.04	35.5	22.6	17.1	28																
S3	<2 mm	0.03	30.9	25.1	14.4	23	0.001	<0.0005				0.79										
S4	<2 mm	0.04	24.5	21.6	12.4	22																
S5	<2 mm	0.02	17.2	22.2	13.4	33	<0.001	<0.0005				0.26										
S6	<2 mm	0.02	19	22.7	12.7	34																
S7	<2 mm	0.02	13.8	16	12.3	29	0.001	<0.0005				0.84										
S8	<2 mm	0.02	15.3	19	12.1	30																
S9	<75 µm	0.15	25	7.3	42.1	51	0.0063	0.009	7.12	2.99	0.06	12.9	0.08	0.07	2.009792	0.849980	35	17.41473	4.6	2.055	0.829	8.34
	<2 mm	0.19	51.6	12.1	70.6	91	0.004	0.0039														
S10	<75 µm	0.11	34.4	10.1	49.6	62	0.0131	0.014							2.026788	0.85523	35.4095	17.47075	7	2.077	0.842	8.78
	<2 mm	0.12	53.7	12	78.5	98	0.002	0.0023														
S11	<75 µm	0.12	33.1	10.8	52.4	61																
	<2 mm	0.15	45.6	13.2	72.3	84																
S12	<75µm	0.13	43.4	7.2	80.3	66									2.024544	0.845278	35.57971	17.57419	6.8	2.061	0.827	8.47
	<2 mm	0.12	64.9	9.6	108	99																
S13	<2 mm	0.13	59.4	9	116	107																
S14	<2 mm	0.13	82.1	12.6	124	116																
S15	<75 µm	0.10	33.6	22.2	22.2	77	0.012	0.0126							2.024385	0.852311	35.8801	17.72395	13.8	2.065	0.834	10.2
S16	<75 µm	0.08	28.7	23.2	19.2	72									2.027438	0.863601	35.66319	17.59028	15.6	2.056	0.836	18.2

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**	**Al_2O_3 (mg/kg)**	**Fe_2O_3 (mg/kg)**	**MnO (mg/kg)**	**C_{org} (wt %)**	**S (wt %)**	**$S_{sulfate}$ (wt %)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**$^{208}Pb/^{204}Pb$**	**$^{206}Pb/^{204}Pb$**	**Total Pb (mg/kg)**	**$^{208}Pb/^{206}Pb$**	**$^{207}Pb/^{206}Pb$**	**Total Pb (mg/kg)**
	Laboratory	ALS	ALS	ALS	ALS	ALS	ALS	ALS	AAC	AAC	AAC	ALS	ALS	ALS	ANSTO	ANSTO	ANSTO	ANSTO	ANSTO	CDU	CDU	CDU
Sample ID	***Sieve fraction***																					
S17	<75 µm	0.05	31.4	21.8	24	75									2.0373	0.8742	35.3391	17.3460	15.2	2.066	0.833	17.7
S18	<75 µm	0.10	37.2	20.6	23.9	77																
S19	<75 µm	0.04	36.2	17.2	25.2	73									2.0268	0.8635	36.0295	17.7762	22.3	2.042	0.822	25.6
S20	<75 µm	0.05	27.7	14.9	18.9	60	0.016	0.012														
S21	<75 µm	0.03	31.4	17.4	20.7	60	0.009	0.0078	13.1	5.67	0.13	3.5	0.18	0.11	2.0268	0.8596	35.3196	17.4261	12.5	2.061	0.824	20.4
S22	<75 µm	0.08	32.4	24	20.8	76									2.0238	0.8527	35.8822	17.7301	15.2	2.069	0.822	15.3
S23	<75 µm	0.06	29.2	18.8	19.5	67									2.0142	0.8606	35.0342	17.3940	10.6	2.062	0.830	18.7
S24	<75 µm	0.03	43.3	26.6	24.6	67	0.018	0.0166							2.0489	0.8702	36.3086	17.7210	19.8	2.069	0.829	17.6
S25	<75 µm	0.07	20.2	29.6	23.9	298	0.01	0.0245	14.2	5.38	0.11	1.9	0.04	0.025	2.0484	0.8641	36.1922	17.6683	18.4	2.090	0.843	18.9

Road runoff water, stream water and rainwater samples

	Cd (µg/L)	**Cu (µg/L)**	**Pb (µg/L)**	**Ni (µg/L)**	**Zn (µg/L)**	**pH**	**EC (µS/cm)**
Laboratory	AAC	AAC	AAC	AAC	AAC	JCU	JCU
Sample ID							
KW1 (Filtered)	≤0.05	6.25	0.146	2.24	104		
KW2 (Filtered)	≤0.05	14.2	0.405	1.49	141		
KW3 (Filtered)	≤0.05	12.6	0.592	1.53	266		
KW4 (Filtered)	≤0.05	3.66	≤0.05	0.220	155		
KW5 (Filtered)	≤0.05	6.65	≤0.05	1.61	101		
KW6 (Filtered)	≤0.05	6.19	4.89	1.60	40.9		
KW6 (Total)	≤0.05	3.24	6.46	0.233	30.7	6.83	33
KW7 (Filtered)	≤0.05	3.79	0.433	0.335	47.6		
KW7 (Total)	≤0.05	6.48	5.84	0.977	77.3	6.76	18
KW8 (Filtered)	≤0.05	1.96	≤0.05	≤0.1	24.1		
KW8 (Total)	≤0.05	3.76	2.06	0.352	36.0	7.03	35
KW9 (Filtered)	≤0.05	2.56	≤0.05	0.595	32.2		
KW9 (Total)	≤0.05	2.86	2.28	0.445	40.0	6.32	9.4
KW10 (Filtered)	≤0.05	9.31	1.52	3.58	1220		
KW10 (Total)	≤0.05	11.7	4.61	2.99	1300	6.25	650
KW11 (Filtered)	≤0.05	13.5	2.30	≤0.1	207		
KW11 (Total)	≤0.05	15.8	7.44	≤0.1	238	7.08	327
KW12 (Filtered)	≤0.05	33.4	4.12	6.53	385		
KW12 (Total)	≤0.05	27.1	9.84	5.31	312	7.42	2074
KW13 (Filtered)	≤0.05	12.9	4.71	≤0.1	169		
KW13 (Total)	≤0.05	25.3	19.8	4.67	342	7.42	496
KW14 (Filtered)	≤0.05	6.71	1.12	≤0.1	82.1		
KW14 (Total)	≤0.05	7.41	4.35	≤0.1	88.2	9.16	1153

	Cd (µg/L)	**Cu (µg/L)**	**Pb (µg/L)**	**Ni (µg/L)**	**Zn (µg/L)**	**pH**	**EC (µS/cm)**
Laboratory	AAC	AAC	AAC	AAC	AAC	JCU	JCU
Sample ID							
KW15 (Filtered)	≤0.05	6.00	1.31	≤0.1	115		
KW15(Total)	≤0.05	4.95	11.3	≤0.1	80.8	6.47	76
KW16 (Filtered)	0.532	109	9.95	20.5	3750		
KW16 (Total)	0.621	108	15.3	20.9	3800	5.6	1866
KW17 (Filtered)	≤0.05	22.9	27.6	6.14	235		
KW17 (Total)	≤0.05	30.9	63.3	6.22	251	6.64	635
KW18 (Filtered)	≤0.05	21.2	2.49	2.44	342		
KW18 (Total)	≤0.05	25.9	13.6	3.12	501	6.37	242
CW1 (Filtered)	≤0.05	4.89	0.704	0.209	50.9		
CW2 (Filtered)	≤0.05	9.42	1.06	1.07	62.3		
CW3 (Filtered)	≤0.05	12.9	0.915	1.99	117		
CW4 (Filtered)	≤0.05	7.46	0.939	0.752	83.7		
CW5 (Filtered)	≤0.05	4.93	0.200	0.288	58.1		
CW5 (Total)	≤0.05	14.7	10.2	1.58	98.3	6.56	18
CW6 (Filtered)	≤0.05	6.06	≤0.05	0.351	65.7		
CW6 (Total)	≤0.05	12.6	7.84	0.761	94.0		
CW7 (Filtered)	≤0.05	6.17	≤0.05	1.70	52.1		
CW7 (Total)	≤0.05	7.67	3.52	0.917	58.7	6.71	13
CW8 (Filtered)	0.934	3.07	≤0.05	0.243	40.4		
CW8 (Total)	≤ 0.05	3.51	2.76	0.577	54.6	6.58	16
CW9 (Filtered)	≤0.05	12.4	1.40	≤ 0.1	559		
CW9 (Total)	≤0.05	25.8	27.1	2.28	853		
CW10 (Filtered)	≤0.05	14.1	1.31	≤0.1	569		
CW10 (Total)	≤0.05	38.9	39.6	4.38	995	6.64	20
CW11 (Filtered)	≤0.05	12.3	1.58	≤0.1	282		
CW11 (Total)	≤0.05	20.4	13.8	≤0.1	369		

	Cd (μg/L)	**Cu (μg/L)**	**Pb (μg/L)**	**Ni (μg/L)**	**Zn (μg/L)**	**pH**	**EC (μS/cm)**
Laboratory	AAC	AAC	AAC	AAC	AAC	JCU	JCU
Sample ID							
CW12 (Filtered)	≤0.05	20.6	1.70	2.84	608		
CW12 (Total)	≤0.05	29.7	10.1	3.91	823		
S_W1 (Filtered)	0.0585	0.908	0.105	0.446	19.9		
S_W1 (Total)	≤0.05	0.940	1.30	0.170	8.29		
S_W2 (Filtered)	0.080	0.717	0.101	≤0.1	11.3		
S_W2 (Total)	≤0.05	0.891	0.646	0.161	≤5		
R_W1						6.03	70
R_W2						6.15	93
R_W3						5.43	92
R_W4						5.75	93
R_W5						5.77	5
R_W6						5.87	6
R_W7						5.99	4

Soil samples

	Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
Laboratory	ALS	ALS	ALS	ALS	ALS
Sample ID					
KT1-i	0.16	75.8	185	44	633
KT2	0.21	53.1	102	38.4	918
KT3-i	0.21	49.1	66.5	32.3	1050
KT4-i	0.49	66.9	109	28.6	1530
KT5	0.17	250	97.3	25.2	729
KT6	0.20	61.1	73.3	25.3	636
KT7-i	0.08	33	35.6	14.6	144
KT1-ii	0.05	54	43.7	13.1	117
KT3-ii	0.01	16.7	20	7.2	54
KT4-ii	0.05	30.2	18.3	24.7	146
KT7-ii	0.06	32.5	14.6	28.2	140
DT1	0.05	7.3	11.2	3.6	21
DT2	0.07	6.6	10.6	5.7	19
DT3	0.12	5.8	10	3.7	55
DT4	0.09	3.1	12.2	3	21
DT5	0.09	4.4	13.2	4	83

Grass samples

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
	Laboratory	AAC	AAC	AAC	AAC	AAC
	Sample ID					
Stem tissue						
	KG1-i	0.060	3.17	14.0	0.71	101
	KG2	0.028	1.85	0.88	1.40	320
	KG3-i	0.028	3.52	0.57	0.51	131
	KG4-i	0.038	1.97	0.77	0.53	289
	KG5	0.055	3.74	1.06	0.73	232
	KG6	0.062	2.73	3.30	1.37	326
	KG7-i	0.050	3.16	4.85	1.60	168
	KG1-ii	0.043	1.92	0.93	0.48	73.3
	KG3-ii	0.028	1.71	0.62	0.29	64.4
	KG4-ii	0.034	2.20	2.26	0.24	65.4
	KG7-ii	0.041	3.75	0.70	0.67	35.6
	DG1	0.257	1.90	1.17	0.17	50.1
	DG2	0.028	6.91	1.02	0.24	18.1
	DG3	0.055	8.90	2.13	0.35	41.1
	DG4	0.078	2.63	1.79	0.42	40.8
	DG5	0.087	2.42	11.08	0.50	37.0

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
	Laboratory	AAC	AAC	AAC	AAC	AAC
	Sample ID					
Root tissue						
	KG1-i	0.126	41	5.80	17.9	153
	KG2	0.159	41.3	2.69	6.83	169
	KG3-i	0.118	18.1	1.65	13.3	224
	KG4-i	0.122	15.7	3.35	5.24	362
	KG5	0.223	37.1	3.40	16	167
	KG6	0.190	27.8	2.73	7.82	183
	KG7-i	0.128	29.1	2.73	6.52	38.8
	KG1-ii	0.172	16.9	2.11	9.65	52.1
	KG3-ii	0.064	12.7	1.40	2.82	22.5
	KG4-ii	0.093	9.33	1.21	4.14	21.2
	KG7-ii	0.088	24.5	6.51	4.93	37.8
	DG1	0.197	5.62	0.64	2.66	22.2
	DG2	0.175	5.98	0.70	4.25	11.5
	DG3	0.131	19.6	0.58	2.09	14.6
	DG4	0.183	4.58	1.21	4.03	22
	DG5	0.658	9.84	2.60	18.5	22.6

Laboratory experiment extracts

	Cd (μg/L)	**Cu (μg/L)**	**Pb (μg/L)**	**Ni (μg/L)**	**Zn (μg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC
Sample ID					
L1	0.38	91.3	17.7	27.8	2370
L2	4.71	194	9.19	65.6	12600
L3	13	585	1530	129	112000
L4	5.16	103	10.9	2.97	119000
L5	20.9	1550	1010	163	94000
L6a	≤0.05	22.4	25.8	10.5	1690
L6b	≤0.05	21.7	67.1	9.63	1510
L6c	≤0.05	18.5	22.4	9.65	1690
L6d	≤0.05	16.1	25.7	8.78	1290
L7a	≤0.05	16.7	39.8	12.2	869
L7b	≤0.05	15.5	83.4	11.4	737
L7c	≤0.05	15.9	40.1	12.7	810
L7d	≤0.05	15.7	37.6	12.7	1570
L8a	11.8	1030	1890	171.0	57100
L8b	12.4	1420	2610	194	61500
L8c	≤0.05	3.09	0.985	≤0.1	≤5
L8d	14.0	1210	1950	181	59900
L9a	19.1	2640	6350	126	43900
L9b	15.3	2570	25000	135	53900
L9c	11.6	2020	13900	114	44800
L9d	15.0	3400	12400	139	48600
L10a	23.9	2300	4780	229	125000
L10b	18.9	3240	3410	213	123000

	Cd (μg/L)	**Cu (μg/L)**	**Pb (μg/L)**	**Ni (μg/L)**	**Zn (μg/L)**	**Al (mg/l)**	**Fe (mg/L)**	**Ca (mg/L)**	**pH**	**Eh (mV)**	**DO (mg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC	AAC	AAC	AAC	JCU	JCU	JCU
Sample ID											
L10c	15.6	1960	3330	188	107000						
L10d	16.8	2670	3930	215	129000						
L11a	27.8	6290	6090	133	70300						
L11b	18.6	15300	10700	145	83200						
L11c	17.4	9870	7490	145	77500						
L11d	15.9	21400	8700	157	76700						
L12	0.02	4.68	22.7	0.23	95.6						
L13	0.04	2.49	10.2	0.42	169						
L14	0.02	3	4.4	0.05	153						
L15	0.09	1.62	1.79	1.03	294						
L16	0.01	4.65	10.2	0.45	104						
L17	0.04	4.15	8.64	0.71	132						
L18	≤0.05	1.05	4.66	0.04	7.46						
L19	≤0.05	2.34	6.21	≤0.1	6.66						
L20	≤0.05	0.31	1.42	0.06	2.61						
L21	≤0.05	0.68	1.01	0.23	21.8						
L22	≤0.05	1.26	0.51	0.21	6.3						
L23	0.01	0.06	1.05	≤0.1	1.57						
L24	≤0.05	2.7	1.39	≤0.1	0.6						
L25	0.03	0.14	1.36	0.14	2.15						
L26	0.01	0.05	0.82	0.02	0.67						
L27	0.01	0.08	1.58	≤0.1	0.91						
L28 (Filtered)	0.154	21.4	3.23	5.49	669	0.116	0.238	13.0			
L28 (Total)	0.160	20.9	5.38	5.71	587	0.0951	0.454	12.9	6.36	186	8.82
L29 (Filtered)	0.220	70.4	6.49	18.4	2060	0.254	0.210	42.1			
L29 (Total)	0.245	76.8	9.89	20.5	2380	0.859	0.468	43.8	6.43	157	8.01
L30 (Filtered)	0.0512	21.5	3.40	5.17	684	0.0793	0.102	8.83			
L30 (Total)	0.0505	21.7	5.42	5.46	627	0.291	0.162	9.72	6.88	143	7.93
L31 (Filtered)	≤0.05	11.5	2.88	2.83	361	0.0353	0.115	5.49			
L31 (Total)	≤0.05	9.54	4.27	2.40	290	0.078	0.208	4.76	7.09	145	7.52

	Cd (μg/L)	**Cu (μg/L)**	**Pb (μg/L)**	**Ni (μg/L)**	**Zn (μg/L)**	**Al (mg/l)**	**Fe (mg/L)**	**Ca (mg/L)**	**pH**	**Eh (mV)**	**DO (mg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC	AAC	AAC	AAC	JCU	JCU	JCU
Sample ID											
L32 (Filtered)	≤0.05	8.09	1.78	1.91	267	0.0187	≤0.1	4.57			
L32 (Total)	≤0.05	8.80	4.20	2.22	272	0.0802	0.158	4.95	7.13	149	7.72
L33 (Filtered)	≤0.05	6.00	1.05	1.53	196	0.0133	≤0.1	3.84			
L33 (Total)	≤0.05	5.98	3.64	1.45	160	0.0324	0.113	3.91	7.15	153	7.87
L34 (Filtered)	≤0.05	5.27	1.46	1.60	167	0.00815	≤0.1	3.77			
L34 (Total)	≤0.05	7.15	6.48	1.35	127	0.0415	≤0.1	3.87	7.16	151	7.93
L35 (Filtered)	≤0.05	4.59	1.41	1.46	146	0.00276	≤0.1	3.44			
L35 (Total)	≤0.05	4.06	7.09	1.13	123	0.0967	≤0.1	≤0.005	7.18	152	7.41
L36 (Filtered)	≤0.05	3.52	1.02	0.988	115	≤0.0005	≤0.1	2.99			
L36 (Total)	≤0.05	3.56	2.90	0.875	119	0.0367	0.223	3.27	7.18	153	7.13
L37 (Filtered)	≤0.05	6.51	1.63	1.82	112	≤0.0005	≤0.1	2.86			
L37 (Total)	≤0.05	2.87	5.47	0.879	86.4	0.124	0.133	2.91	7.17	154	7.84
L38 (Filtered)	0.346	46.9	8.33	8.14	1180	0.0983	0.163	10.7			
L38 (Total)	0.290	54.4	40.8	10.1	1160	1.96	2.73	10.9	6.44	158	6.24
L39 (Filtered)	0.348	38.4	4.47	4.06	847	0.0649	0.145	7.72			
L39 (Total)	0.174	45.0	24.5	6.11	855	1.38	2.02	7.75	6.78	147	5.95
L40 (Filtered)	0.177	32.8	4.67	4.16	651	0.0396	0.122	6.52			
L40 (Total)	0.101	38.1	16.8	5.41	644	0.753	0.989	6.48	6.82	144	5.86
L41 (Filtered)	0.203	12.5	2.37	0.687	280	0.024	≤0.1	2.81			
L41 (Total)	0.136	16.1	11.1	1.61	273	0.478	0.990	2.88	6.87	144	5.14
L42 (Filtered)	0.173	9.80	1.77	≤0.1	164	0.0233	≤0.1	1.76			
L42 (Total)	0.126	16.4	25.0	1.79	231	1.22	1.61	2.21	7.12	140	5.29
L43 (Filtered)	0.196	4.60	1.12	≤0.1	91.1	0.0129	≤0.1	1.06			
L43 (Total)	0.0828	14.1	29.5	1.80	201	1.62	2.30	1.63	7.17	149	5.80
L44 (Filtered)	0.188	5.40	1.31	≤0.1	124	0.0124	≤0.1	1.74			
L44 (Total)	0.171	12.9	16.2	2.66	220	1.11	1.49	2.01	7.11	153	5.74
L45 (Filtered)	0.168	3.15	0.882	≤0.1	74.0	0.0118	≤0.1	1.05			
L45 (Total)	0.0781	8.04	17.3	1.25	131	0.57	1.17	1.31	7.28	158	5.11
L46 (Filtered)	0.101	2.59	0.706	≤0.1	67.3	0.0124	≤0.1	0.945			
L46 (Total)	0.0958	10.5	21.6	1.98	132	0.924	1.33	1.26	7.31	171	5.05

	Cd (µg/L)	**Cu (µg/L)**	**Pb (µg/L)**	**Ni (µg/L)**	**Zn (µg/L)**	**Al (mg/L)**	**Fe (mg/L)**	**Ca (mg/L)**	**pH**	**Eh (mV)**	**DO (mg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC	AAC	AAC	AAC	JCU	JCU	JCU
Sample ID											
L47 (Filtered)	0.166	4.29	1.15	≤0.1	87.4	0.0117	≤0.1	1.34			
L47 (Total)	0.463	15.7	33.0	3.87	225	1.69	2.58	1.94	7.31	162.00	5.13
L48 (Filtered)	≤ 0.05	5.46	1.06	2.47	189	0.017	≤0.1	3.03			
L48 (Total)	0.0918	20.1	49.4	9.23	540	3.92	3.86	5.72	6.41	263.00	5.15
L49 (Filtered)	0.0884	17.7	2.33	6.82	647	0.0236	≤0.1	12.3			
L49 (Total)	0.0902	25.2	26.2	10.3	692	1.52	1.08	13.1	6.42	208	4.61
L50 (Filtered)	0.107	15.1	3.33	16.3	1390	0.0803	≤0.1	28.5			
L50 (Total)	0.104	18.6	7.58	17.9	1120	0.21	0.189	29.4	5.98	78	1.73
L51 (Filtered)	0.0878	4.40	3.24	39.8	1080	0.0929	0.704	91.5			
L51 (Total)	0.0871	6.59	6.10	36.6	1310	0.27	1.02	82.8	6.77	105	0.95
L52 (Filtered)	0.202	9.75	0.742	13.8	201	0.0134	0.593	63.5			
L52 (Total)	0.362	10.5	5.04	12.9	470	0.07	4.55	89.9	7.04	52	1.94
L53 (Filtered)	0.618	37.2	2.15	6.56	1130	0.0911	0.244	8.18			
L53 (Total)	1.20	148	203	60.7	5080	14.5	20.2	17.3	6.54	98	5.85
L54 (Filtered)	0.976	42.1	2.85	11.3	1070	0.0702	0.214	8.83			
L54 (Total)	1.05	128	171	24.6	3430	9.84	13.1	15.6	6.53	93	5.92
L55 (Filtered)	0.519	43.1	≤0.05	12.2	1200	0.0447	0.233	14.5			
L55 (Total)	0.693	76.4	80.6	18.1	2160	4.77	6.14	17.9	6.55	80	3.13
L56 (Filtered)	0.264	16.4	≤0.05	12.8	842	0.0299	0.194	10.5			
L56 (Total)	0.272	38.5	16.5	9.01	1030	1.12	1.54	12.2	6.78	55	2.7
L57 (Filtered)	0.374	3.88	≤0.05	11.7	1080	0.0136	0.664	24.1			
L57 (Total)	0.215	11.2	8.01	6.84	909	0.634	1.41	16.6	7.1	46	2.26
L58 (Filtered)	1.41	48.5	103	102	753	0.0255	0.432	19.2			
L58 (Total)	0.302	16.5	9.33	8.94	824	0.473	1.38	19.3	7.26	51	2.09
L59 (Filtered)	0.289	9.37	0.650	5.52	292	0.0166	0.232	25.6			
L59 (Total)	0.250	15.5	11.0	7.00	391	0.334	0.714	25.2	7.33	69	3.98
L60 (Filtered)	0.196	4.58	1.58	4.07	229	0.0129	0.13	16.1			
L60 (Total)	0.199	7.68	5.27	5.01	247	0.07	0.252	15.8	7.18	71	4.01
L61 (Filtered)	0.191	5.58	0.729	4.16	184	0.0159	0.299	18.6			
L61 (Total)	0.233	20.0	36.2	6.47	446	1.16	2.31	19.1	7.24	76	4.05

	Cd (µg/L)	**Cu (µg/L)**	**Pb (µg/L)**	**Ni (µg/L)**	**Zn (µg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC
Sample ID					
L62	≤ 0.05	475	6.2	58	912
L63	≤ 0.05	65	1.1	8	1120
L64	≤ 0.05	32	1.2	4	2430
L65	≤ 0.05	15	1.2	6	7890
L66	≤ 0.05	2	1.4	17	1300
L67	≤ 0.05	84	4.2	8.1	513
L68	≤ 0.05	32	1.1	1	598
L69	≤ 0.05	12	1	4.1	1880
L70	≤ 0.05	4	1	6.1	5780
L71	≤ 0.05	2	0.9	5.9	6200
L72 – stem	0.025	6.3	2.4	1	552
L72 – root	0.080	86	2.1	3.3	105
L73 – stem	0.075	3.9	3.4	1.2	1250
L73 – root	0.180	122	2.9	6.3	225
L74 – stem	0.16	5.2	0.45	1.24	1210
L74 – root	0.200	54	6.7	2.1	254
L75	0.40	99.9	18.6	21.9	2260
L76	0.32	96.2	20.7	20.7	786
L77	0.51	124	17.4	28.9	2830
L78	1.02	115	21	25.1	1070
L79	0.44	73.9	19.1	23.4	2370
L80	0.33	64.9	27.8	21.9	377
L81	0.298	68.1	6.97	≤0.1	2110
L82	≤0.05	52	2.74	≤0.1	506
L83	0.3	65.4	6.54	≤0.1	2090
L84	≤0.05	43	1.46	≤0.1	307
L85	0.26	69.8	6.42	≤0.1	2610

	Cd (µg/L)	**Cu (µg/L)**	**Pb (µg/L)**	**Ni (µg/L)**	**Zn (µg/L)**
Laboratory	AAC	AAC	AAC	AAC	AAC
Sample ID					
L86	≤0.05	46.9	0.903	≤0.1	214
L87	0.53	93.8	28	15.4	2750
L88	0.72	50.3	10.3	11.1	202
L89	1.28	153	47.1	35.7	4050
L90	0.5	52.9	6	10.8	180

Composite samples

			Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
		Laboratory	ALS	ALS	ALS	ALS	ALS
		Replicates/subsamples					
Sample ID	***Experiment used in***						
KRC$_M$1	Sieving, column-leach and ponding	Replicate no. 1	0.17	46	54.2	62.7	779
		Replicate no. 2	0.18	45.6	54.9	59.3	742
		Replicate no. 3	0.17	44.9	56.1	61.8	807
		Mean value	*0.17*	*45.5*	*55.1*	*61.3*	*776*
		Standard deviation	*0.006*	*0.56*	*0.96*	*1.76*	*32.6*
CRC$_M$1	Sieving, column-leach and ponding	Replicate no. 1	0.2	57.1	165	39.5	571
		Replicate no. 2	0.22	77.5	161	38	578
		Replicate no. 3	0.19	58.3	162	40.2	582
		Mean value	*0.2*	*64.3*	*163*	*39.2*	*577*
		Standard deviation	*0.015*	*11.5*	*2.08*	*1.12*	*5.57*
KRC$_M$2	Sieving, remediation experiments	Replicate no. 1 (<2 mm)	0.19	33.5	50.7	45.5	1220
		Replicate no. 2 (<2 mm)	0.17	36.6	49.5	45.3	1230
		Replicate no. 3 (<2 mm)	0.18	32.6	48.3	43.8	1420
		Mean value	*0.18*	*34.2*	*49.5*	*44.9*	*1290*
		Standard deviation	*0.01*	*2.1*	*1.2*	*0.93*	*113*
CRC$_M$2	Sieving	Replicate no. 1 (<2 mm)	0.64	54.3	95.6	34	666
		Replicate no. 2 (<2 mm)	0.59	84.5	96.5	34.3	608
		Replicate no. 3 (<2 mm)	0.57	160	94.7	35.6	613
		Mean value	*0.6*	*99.6*	*95.6*	*34.6*	*629*
		Standard deviation	*0.036*	*54.4*	*0.9*	*0.85*	*32.1*

			Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**
		Laboratory	ALS	ALS	ALS	ALS	ALS
		Replicates/subsamples					
KRC$_{M}$3	Sieving, sequential extraction, citrate-dithionite extraction, bioavailable extractions	Replicate no. 1 (<250 µm)	0.33	77.3	60.1	35.5	2860
		Replicate no. 2 (<250 µm)	0.31	108	48.2	32.4	2790
		Replicate no. 3 (<250 µm)	0.32	65.8	53.7	32.7	2760
		Mean value	*0.32*	*83.7*	*54*	*33.5*	*2800*
		Standard deviation	*0.01*	*21.8*	*5.96*	*1.71*	*51.3*
		Replicate no. 1 (<500 µm)	0.27	91	66	34	1920
		Replicate no. 1 (<2 mm)	0.36	53.4	62	35.3	1380
		Replicate no. 2 (<2 mm)	0.37	67.6	60.1	37.2	1310
		Replicate no. 3 (<2 mm)	0.26	42	62.9	38.4	1200
		Replicate no. 4 (<2 mm)	0.46	54.4	79.5	42.2	1430
		Mean value	*0.36*	*54.4*	*66.1*	*38.3*	*1330*
		Standard deviation	*0.082*	*10.5*	*8.99*	*2.91*	*101*
KRC$_{M}$3	Sieving, citrate-dithionite extraction, bioavailable extractions	Replicate no. 1 (<500 µm)	0.27	110	119	43.6	837
		Replicate no. 1 (<2 mm)	0.28	64.6	91.5	45.4	691
		Replicate no. 2 (<2 mm)	0.32	90.4	120	39.3	780
		Replicate no. 3 (<2 mm)	0.27	125	107	44.9	687
		Replicate no. 4 (<2 mm)	0.26	144	108	41.7	679
		Mean value	*0.28*	*106*	*107*	*42.8*	*709*
		Standard deviation	*0.026*	*35.2*	*11.7*	*2.87*	*47.4*

Road sediment sieve fractions

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**C$_{org}$ (wt %)**
Laboratory		ALS	ALS	ALS	ALS	ALS	ALS
Source	***Sample ID***						
KRC$_M$1	KR$_F$1	0.17	67.2	94.5	51.1	421	
	KR$_F$2	0.23	65.2	96.5	49.5	796	
	KR$_F$3	0.28	77.0	89.2	76.8	982	
	KR$_F$4	0.33	63.5	92.6	57.7	1780	
	KR$_F$5	0.37	55.5	100	44.9	2220	
	KR$_F$6	0.28	73.0	77.0	44.8	1480	
	KR$_F$7	0.15	41.1	48.6	43.7	403	
	KR$_F$8	0.10	32.8	21.5	53.2	162	
	KR$_F$9	0.09	35.9	19.4	70.6	134	
	KR$_F$10	0.07	29.5	12.1	65.6	77	
CRC$_M$1	CR$_F$1	0.5	150	188	72.4	1430	
	CR$_F$2	0.4	127	209	77.4	1560	
	CR$_F$3	0.5	151	245	70.2	1700	
	CR$_F$4	0.4	108	260	51.5	1570	
	CR$_F$5	0.5	112	307	45.1	1010	
	CR$_F$6	0.3	57.7	178	28.1	357	
	CR$_F$7	<0.1	30.7	73.7	32.5	184	
	CR$_F$8	<0.1	17.5	9.8	39.6	91	
	CR$_F$9	<0.1	18.7	10.5	52.1	76	
	CR$_F$10	<0.1	21.1	16.5	62.1	79	
KRC$_M$2	KR$_F$11	0.39	156	195.5	64.6	1420	
	KR$_F$12	0.42	117	176	42.6	2310	16
	KR$_F$13	0.51	76.7	125	32.4	4010	22.3
	KR$_F$14	0.1	43.3	57.5	33.2	630	3.81
	KR$_F$15	0.06	33.4	26.6	89.3	138	0.87

		Cd (mg/kg)	**Cu (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Zn (mg/kg)**	**Pd (mg/kg)**	**Pt (mg/kg)**	**C$_{org}$ (wt %)**
Laboratory		ALS	ALS	ALS	ALS	ALS	ALS	ALS	ALS
Source	***Sample ID***								
CRC$_M$2	CR$_F$11	0.68	116	192	41.8	1490			12
	CR$_F$12	0.42	70	238	54.9	1570			10.9
	CR$_F$13	0.25	139	200	39.9	1150			9.38
	CR$_F$14	0.05	17.7	26.1	27.6	229			0.92
	CR$_F$15	0.04	24.7	11.2	70.1	104			0.55
KRC$_M$3	KR$_F$16						0.124	0.19	
	KR$_F$17						0.063	0.153	8.4
	KR$_F$18						0.068	0.207	5.8
	KR$_F$19						0.014	0.0647	
CRC$_M$3	CR$_F$16						0.052	0.0848	
	CR$_F$17						0.089	0.108	2
	CR$_F$18						0.194	0.232	11.2
	CR$_F$19						0.053	0.0418	1

Appendix C – Laboratory extraction procedures

Sequential extraction method (from Tessier et al. 1979)

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THIS TEXT HAS BEEN REMOVED DUE TO COPYRIGHT RESTRICTIONS

Citrate-dithionite oxide extraction (from Rayment and Higginson, 1992)

THIS TEXT HAS BEEN REMOVED DUE TO COPYRIGHT RESTRICTIONS

Bioavailable extractions (from Rayment and Higginson, 1992)

Appendix D – Quality control

Duplicates

		Cd	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**	**Al**	**Ca**	**Fe**
Sample ID	***Description***										
QC1 (mg/kg)	Duplicate of KR22	0.29	40.1	33.9	39.3	2830					
	KR22	0.31	41.3	24.8	39.5	2810					
	RPD	**6.67**	**2.95**	**-31**	**0.51**	**-0.71**					
QC2 (mg/kg)	Duplicate of KT3-i	0.16	114	90.3	24.9	868	0.024	0.0288			
	KT3-i	0.21	49.1	66.5	32.3	1050	0.016	0.0319			
	RPD	**27**	**-79**	**-30.4**	**25.9**	**18.5**	**-40**	**10.2**			
QC3 (µg/L)	Duplicate of L31 (Filtered)	< 0.05	11.2	2.75	2.67	362			35.4	5420	<100
	L31 (Filtered)	< 0.05	11.5	2.88	2.83	361			35.3	5490	115
	RPD	**0**	**2.64**	**4.62**	**5.82**	**-0.28**			**-0.28**	**1.28**	**14**
QC4 (µg/L)	Duplicate of L31 (Total)	< 0.05	8.77	7.07	2.36	260			66.3	4630	178
	L31 (Total)	< 0.05	9.54	4.27	2.40	290			78.2	4760	208
	RPD	**0**	**8.41**	**-49.4**	**1.68**	**10.9**			**16.5**	**2.77**	**15.5**
QC5 (µg/L)	Duplicate of L34 (filtered)	0.212	5.35	1.38	<0.1	126			27.7	1680	<100
	L34 (filtered)	0.188	5.40	1.31	<0.1	124			12.4	1740	<100
	RPD	**-12**	**0.93**	**-5.2**	**0**	**-1.6**			**-76.3**	**3.51**	**0**

		Cd	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**	**Al**	**Ca**	**Fe**	**208Pb/206Pb***	**207Pb/206Pb***	C_{org}
Sample ID	***Description***													
QC6 (µg/L)	Duplicate of L34 (total)	0.149	14.6	23.4	4.06	209			1250	2080	1840			
	L34 (total)	0.171	12.9	16.2	2.66	220			1110	2010	1490			
	RPD	**13.8**	**-12.4**	**-36.4**	**-41.7**	**5.13**			**-11.9**	**-3.42**	**-21**			
QC7 (µg/L)	Duplicate of L52 (filtered)	0.203	9.76	0.968	13.8	209			14.0	62700	578			
	L52 (filtered)	0.202	9.75	0.742	13.8	201			13.4	63500	593			
	RPD	**-0.49**	**-0.10**	**-26.4**	**0**	**-3.9**			**-4.38**	**1.27**	**2.56**			
QC8 (µg/L)	Duplicate of L52 (total)	0.31	12.5	7.68	13.5	416			116	77600	3980			
	L52 (total)	0.362	10.5	5.04	12.9	470			73.5	89900	4550			
	RPD	**15.3**	**-17.**	**-41.5**	**-4.48**	**12.2**			**-44.8**	**14.7**	**13.4**			
QC9 (µg/L)	Duplicate of L57 (filtered)	0.351	4.06	< 0.05	11.2	1190			15.0	26700	772			
	L57 (filtered)	0.374	3.88	< 0.05	11.7	1080			13.6	24100	664			
	RPD	**6.34**	**-4.53**	**0**	**4.37**	**-9.69**			**-9.79**	**-10.2**	**-15**			
QC10 (µg/L)	Duplicate of L57 (total)	0.283	9.21	5.29	6.78	754			499	14000	1150			
	L57 (total)	0.215	11.2	8.01	6.84	909			634	16600	1410			
	RPD	**-27.3**	**19.5**	**40.9**	**0.88**	**18.6**			**23.8**	**17**	**20.3**			
QC11 (mg/kg)	Duplicate of S15			10.4								2.0589	0.8272	
	S15			10.2								2.0652	0.8340	
	RPD			**-1.94**								**0.31**	**0.82**	
QC12 (mg/kg)	Duplicate of CR$_F$5	0.2	118	238	42.6	1070								
	CR$_F$5	0.5	112	307	45.1	1010								
	RPD	**85.7**	**-5.22**	**25.3**	**5.70**	**-5.77**								
QC13 (mg/kg)	Duplicate of KR$_F$13	0.44	72.4	127	32.3	3340	0.178	0.324						20.7
	KR$_F$13	0.51	76.7	125	32.4	4010	0.14	0.254						22.3
	RPD	**14.7**	**5.77**	**-1.19**	**0.31**	**18.23**	**-23.9**	**-24.2**						**7.44**

Sample ID	***Description***	**Cd**	**Cu**	**Pb**	**Ni**	**Zn**	**Pd**	**Pt**	**208Pb/206Pb***	**207Pb/206Pb***	**208Pb/204Pb***	**206Pb/204Pb***	C_{org}
QC14 (mg/kg)	Duplicate of $\mathrm{CR_F}$13	0.29	163	155	34.5	1560	0.142	0.284					7.29
	$\mathrm{CR_F}$13	0.25	139	200	39.9	1150	0.239	0.216					9.38
	RPD	**-14.8**	**-15.60**	**25.7**	**14.5**	**-29.9**	**50.9**	**-27.2**					**25.1**
QC15 (mg/kg)	Duplicate of S16			15.6					2.030183	0.858355	35.65835	17.5641	
	S16			15.6					2.027438	0.8636	35.66319	17.59028	
	RPD			**0**					**0.14**	**-0.6**	**0.01**	**0.15**	

Blanks

Sample ID	Laboratory/technique	Sample description	Cd	Cu	Pb	Ni	Zn	Al	Ca	Fe
QC17 (µg/L)	AAC/ICP-AES	DTPA blank	≤0.5	4	6	10	40			
QC18 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand, unsieved	≤0.01	≤0.2	≤0.2	≤0.2	≤2			
QC19 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand, sieved	≤0.01	1.2	0.5	2.8	≤2			
QC20 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand, uncrushed	0.01	2.6	0.9	5	4			
QC21 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand, crushed	0.01	2	4.9	4	4			
QC22 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	30	≤10	≤10	50			
QC23 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	60	≤10	≤10	40			
QC24 (µg/L)*	ALS/ICP-AAS	EDTA blank	≤10	≤10	≤10	≤10	20			
QC25 (µg/L)*	ALS/ICP-AAS	Acetate solution	≤10	≤10	≤10	60	70			
QC26 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	20	10	≤10	90			
QC27 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	≤10	≤10	≤10	30			
QC28 (µg/L)*	ALS/ICP-AAS	EDTA blank	90	20	100	10	60			
QC29 (µg/L)*	ALS/ICP-AAS	Acetate solution	≤10	≤10	30	60	50			
QC30 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	≤10	30	≤10	40			
QC31 (µg/L)*	ALS/ICP-AAS	DTPA blank	≤10	≤10	80	180	10			
QC32 (µg/L)	AAC/ICP-AES	DTPA blank	0.12	2.56	0.934	19.6	28.8			
QC33 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand	≤0.01	2.1	0.6	2.9	≤2			
QC34 (mg/kg)	ALS/ ICP-MS and AES	Cape Flattery sand, oven-dried	≤0.01	2.3	0.5	3.4	≤2			
QC35 (µg/L)	AAC/ ICP-MS and AES	Distilled water	0.0516	1.30	≤0.05	0.581	≤5	≤0.5	≤5	≤100
QC36 (µg/L)	AAC / ICP-MS and AES	Distilled water	0.0623	1.52	5.41	0.580	≤5	≤0.5	84.6	≤100
QC37 (µg/L)	AAC / ICP-MS and AES	Distilled water	0.0987	1.61	2.48	≤0.1	45.7	7.94	42	≤100
QC38 (µg/L)	AAC / ICP-MS and AES	Distilled water	0.178	2.91	1.18	≤0.1	33.8	2.15	116	≤100
QC39 (µg/L)	AAC / ICP-MS and AES	Distilled water	≤ 0.05	≤0.1	≤0.05	≤0.1	≤5	≤0.5	37.9	≤100
QC40 (µg/L)	AAC / ICP-MS and AES	Distilled water	0.0590	3.16	≤0.05	0.724	21.6	≤0.5	56	≤100
QC41 (µg/L)	AAC / ICP-MS and AES	Distilled water	≤ 0.05	3.07	0.558	3.46	33.7	51.8	448	≤100
QC42 (µg/L)	AAC / ICP-MS and AES	Distilled water	≤ 0.05	6.47	1.72	4.52	28.7	10.5	515	≤100

*Sample analysed by ICP-AAS at ALS, Brisbane

Sample ID	Laboratory	Sample description	Cd	Cu	Pb	Ni	Zn	Al	Ca	Fe
QC43 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤ 0.05	≤0.1	≤0.05	≤0.1	≤5	≤0.5	≤100	≤100
QC44 (μg/L)	AAC / ICP-MS and AES	Spike using uncleaned filter equip.	0.0995	11.9	≤0.05	5.00	99.3	≤0.5	124	≤100
QC45 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.436	1.32	≤0.05	0.933	6.26	61.4	10.9	≤100
QC46 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	≤0.1	2.28	0.233	≤5	3.18	≤5	≤100
QC47 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.170	0.474	≤0.1	0.732	≤5			
QC48 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.5	1.75	1.87	0.667	≤5			
QC49 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	≤0.1	0.313	≤0.1	≤5			
QC50 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	0.502	0.376	0.383	≤5			
QC51 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.0900	≤0.1	0.498	0.230	16.2			
QC52 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.133	0.454	0.864	0.644	18.3			
QC53 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	0.847	0.757	3.85	≤5	1.60	≤5	≤50
QC54 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	0.790	1.50	0.374	≤5			
QC55 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.145	≤0.1	≤0.05	0.378	5.50			
QC56 (μg/L)	AAC / ICP-MS and AES	Distilled water (confirmed contamination with lab)	1.01	6.10	72.4	9.75	175			
QC57 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	≤0.1	0.207	≤0.1	≤5			
QC58 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	≤0.1	1.24	0.149	≤5			
QC59 (μg/L)	AAC / ICP-MS and AES	Distilled water	≤0.05	≤0.1	≤0.05	≤0.1	≤5			
QC60 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.688	1.88	2.64	0.181	18.0			
QC61 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.123	2.14	7.67	0.943	10.6			
QC62 (mg/kg)	ALS / ICP-MS and AES	Cape Flattery sand	≤0.01	2.8	0.5	4.8	3			
QC63 (mg/kg)	ALS / ICP-MS and AES	Cape Flattery sand	≤0.01	3.1	0.6	4.2	4			
QC64 (μg/L)	AAC / ICP-MS and AES	Distilled water	0.152	2.05	2.51	0.902	18.5			
QC65 (μg/L)	AAC / ICP-AES	Distilled water	≤0.5	13.1	≤0.5	≤1	≤5			
QC66 (μg/L)	AAC / ICP-AES	MgCl solution	≤0.5	10.7	≤0.5	3.8	≤5			
QC67 (μg/L)	AAC / ICP-AES	Sodium acetate solution	≤0.5	2.06	≤0.5	1.16	≤5			
QC68 (μg/L)	AAC / ICP-AES	Citrate-dithionite solution	≤0.5	≤1	≤0.5	≤1	≤5			
QC69 (μg/L)	AAC / ICP-AES	Nitric acid-peroxide solution	≤0.5	≤1	≤0.5	≤1	≤5			
QC70 (μg/L)	AAC / ICP-AES	Distilled water	≤0.5	≤1	≤0.5	≤1	≤5	≤0.5		≤1000
QC71 (μg/L)	AAC / ICP-AES	Distilled water	≤0.5	≤1	≤0.5	≤1	≤5	≤0.5		≤1000

Standards

Sample ID	***Sample description***	**Cd**	**Cu**	**Pb**	**Ni**	**Zn**
QC72 (mg/kg)	Sample of GXR-3	0.52	24.5	23.1	54.7	325
QC73 (mg/kg)	Sample of GXR-3	0.28	16.8	13.6	44.5	178
QC74 (mg/kg)	Sample of GXR-3	0.29	11.2	13.8	48.7	188
QC75 (mg/kg)	Sample of GXR-3	0.3	10.6	12.1	45.6	192
QC76 (mg/kg)	Sample of GXR-3	0.28	10.6	12	40.4	192
QC77 (mg/kg)	Sample of GXR-3	0.31	11.3	14.2	43.6	154
QC78 (mg/kg)	Sample of GXR-3	0.32	12	14.7	49.8	232

Appendix E - Identification of grasses by the Queensland Herbarium

Queensland Herbarium
Environmental Protection Agency

Botanical Specimens for Identification

Complete this form (one for **each** specimen)
and send with specimen/s to:

Botanical Advisory Service
Queensland Herbarium, EPA
Brisbane Botanic Gardens Mt Coot-tha
Mt Coot-tha Road,
TOOWONG QLD 4066

Office Use

Recd.
Ident.
Desp.
Our Ref.:

Name: Chris Pratt
Company / Department: **James Cook University, Cairns, School of Earth Sciences**
Postal Address **McGregor Road, Smithfield, Cairns**
Postcode 4878
Telephone: **4042 1209** **Fax:**
email: **chris.pratt@jcu.edu.au**

Please send results by ☐ post X☐ email ☐ fax ☐ telephone

Purpose of identification (e.g. commercial consultancy, suspected poisonous, possible weed etc)

Research purposes, part of field study into heavy metal uptake by roadside grasses

Information required **Identification to species level**

Label Information: *Specimens sent to the Queensland Herbarium for identification are frequently retained in the collection for scientific research and geographic distribution records. The label information below when accompanying **each** specimen aids the identification process and greatly increases the scientific value of the specimen.*

Collector's Name & No.: Chris Pratt – ***Specimen CP2*** **Date of collection** 26 May 2004

Locality (include distance to nearest town) Henrys Lookout on Kuranda Range Road, approximately 20 kms from Cairns

Latitude 16 º 51 ' "S **Longitude** 145 º 40 ' "E **Pastoral District**:

Or **Map and grid reference** (eg 9442 333 666)

Or **AMG Coordinates** (Zone, Easting, Northing)

Geodetic System Used (GPS systems): e.g. AGD84, AGD66, WGS84, GDA94

Situation (e.g. plain, creekbank, mountain) Mountain range

Soil/Geology Weathered granite soils mixed with colluvial material from sedimentary units

Vegetation Type (e.g. forest, heath, cultivation, RE number) Grassy field in open eucalypt forest

Kind of plant (e.g. tree, vine, herb) grass

Description (e.g. size, bark type, flower or fruit colour, frequency) Specimens approximately 0.60 - 0.80 metres in length, red/pink to white v or u-shaped flowers with yellow seeds

Abundance Common adjacent to road edges

Other Notes

Botanical Specimens for Identification

Complete this form (one for **each** specimen) and send with specimen/s to:

Botanical Advisory Service
Queensland Herbarium, EPA
Brisbane Botanic Gardens Mt Coot-tha
Mt Coot-tha Road,
TOOWONG QLD 4066

Office Use

Recd.

Ident.

Desp.

Our Ref.:

Name: Chris Pratt

Company / Department: **James Cook University, Cairns, School of Earth Sciences**

Postal Address **McGregor Road, Smithfield, Cairns**

Postcode 4878

Telephone: **4042 1209** **Fax:**

email: **chris.pratt@jcu.edu.au**

Please send results by ☐ post X☐ email ☐ fax ☐ telephone

Purpose of identification (e.g. commercial consultancy, suspected poisonous, possible weed etc)

Research purposes, part of field study into heavy metal uptake by roadside grasses

Information required **Identification to species level**

Label Information: *Specimens sent to the Queensland Herbarium for identification are frequently retained in the collection for scientific research and geographic distribution records. The label information below when accompanying* ***each*** *specimen aids the identification process and greatly increases the scientific value of the specimen.*

Collector's Name & No.: Chris Pratt – ***Specimen CP1*** **Date of collection** 26 May 2004

Locality (include distance to nearest town) Davies Creek Road, 20 kms to Kuranda. 15 kms to Mareeba

Latitude 16 º 59 ‘ “S **Longitude** 145 º 33 ‘ “E **Pastoral District**:

Or **Map and grid reference** (eg 9442 333 666)

Or **AMG Coordinates** (Zone, Easting, Northing)

Geodetic System Used (GPS systems): e.g. AGD84, AGD66, WGS84, GDA94

Situation (e.g. plain, creekbank, mountain) Plain, abandoned field

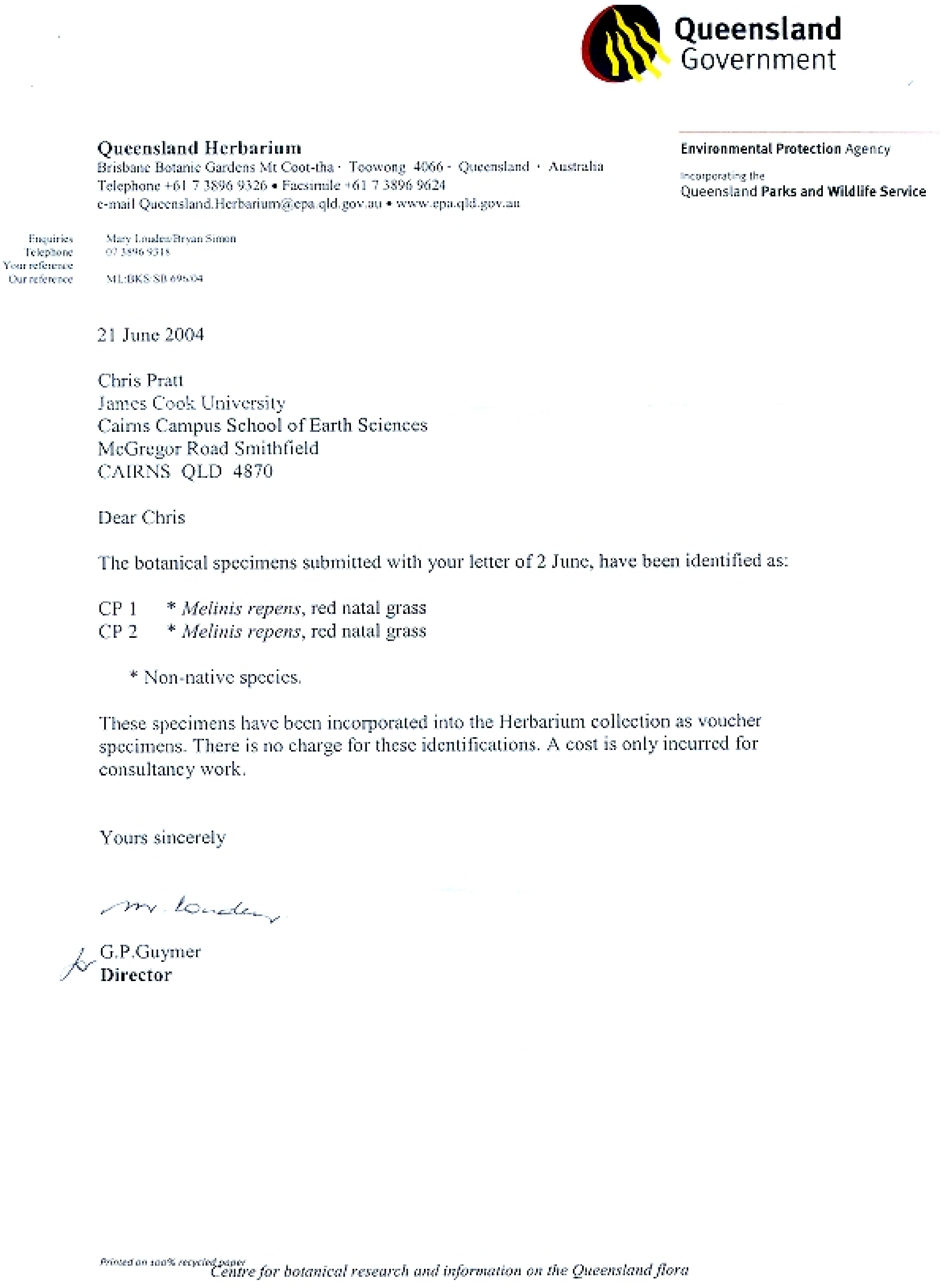
Soil/Geology Sandy soils on top of sodic granite

Vegetation Type (e.g. forest, heath, cultivation, RE number) Grassy field in open eucalypt forest

Kind of plant (e.g. tree, vine, herb) grass

Description (e.g. size, bark type, flower or fruit colour, frequency) Specimens approximately 0.60 - 0.80 metres in length, pink to white v or u-shaped flowers with yellow seeds

Abundance Common in field



Queensland Government

Queensland Herbarium
Brisbane Botanic Gardens Mt Coot-tha · Toowong 4066 · Queensland · Australia
Telephone +61 7 3896 9326 • Facsimile +61 7 3896 9624
e-mail Queensland.Herbarium@epa.qld.gov.au • www.epa.qld.gov.au

Environmental Protection Agency
Incorporating the
Queensland **Parks and Wildlife Service**

Enquiries Mary Louden/Bryan Simon
Telephone 07 3896 9318
Your reference
Our reference ML:BKS:SB 696/04

21 June 2004

Chris Pratt
James Cook University
Cairns Campus School of Earth Sciences
McGregor Road Smithfield
CAIRNS QLD 4870

Dear Chris

The botanical specimens submitted with your letter of 2 June, have been identified as:

CP 1 * *Melinis repens*, red natal grass
CP 2 * *Melinis repens*, red natal grass

* Non-native species.

These specimens have been incorporated into the Herbarium collection as voucher specimens. There is no charge for these identifications. A cost is only incurred for consultancy work.

Yours sincerely

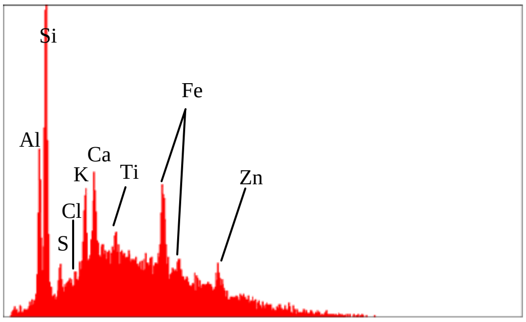
m. Louden

G.P.Guymer
Director

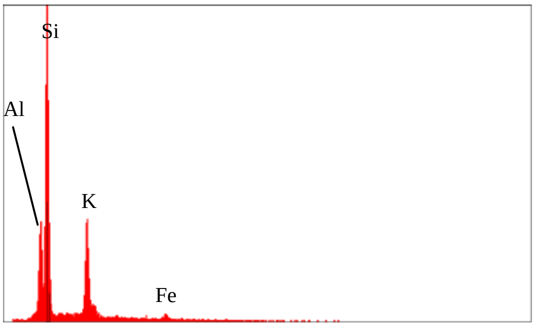
Appendix F – Traffic count data

Appendix G – SEM/EDS and XRD results

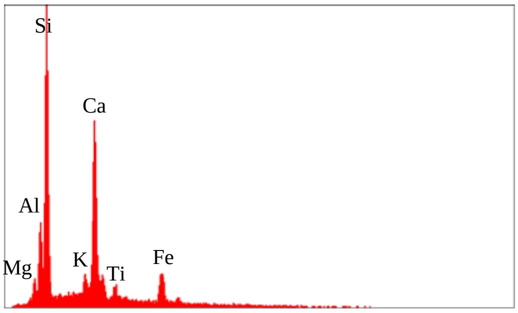
EDS peaks for various particles in the road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts



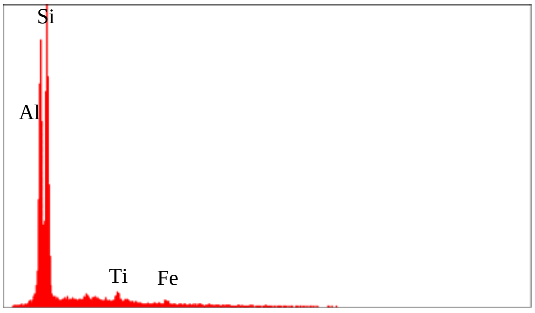
Tyre rubber



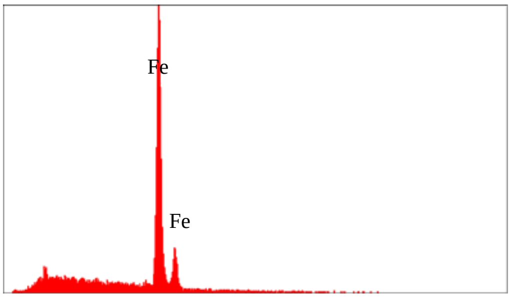
K-feldspar



Plagioclase feldspar

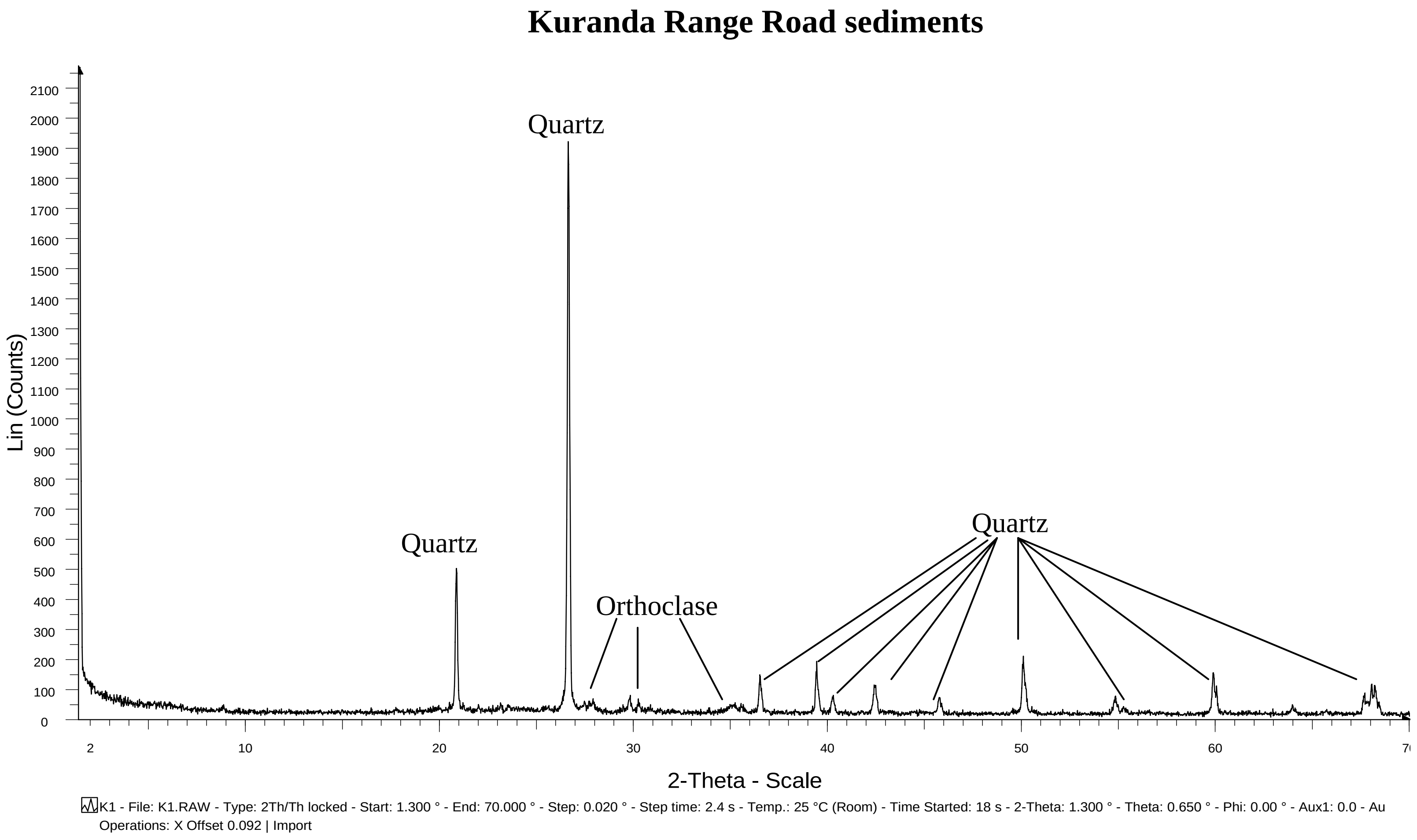


Reflective glass bead

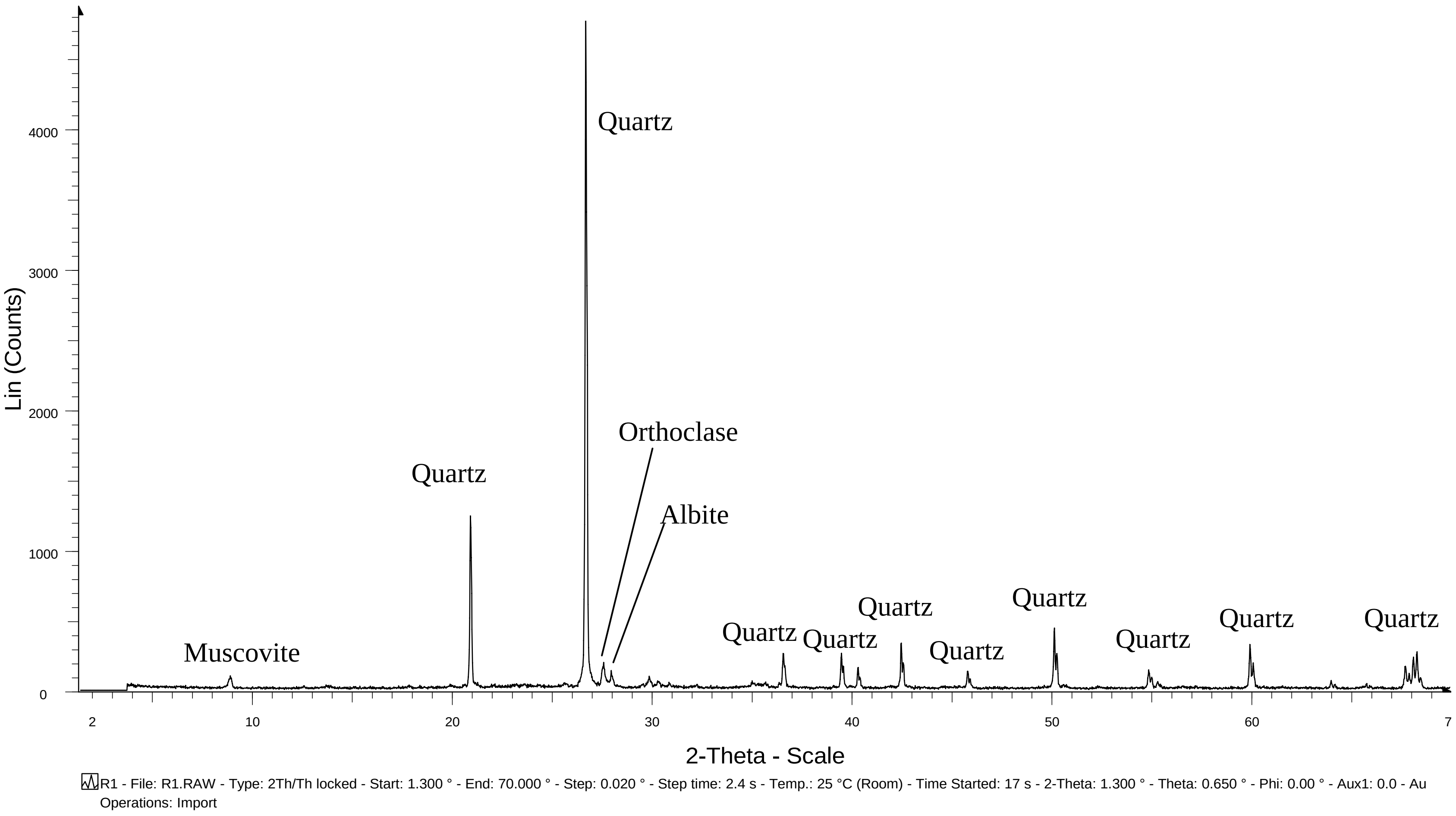


Metal shaving

XRD peaks for road sediments from the Kuranda Range Road and Captain Cook Highway roundabouts



Captain Cook Highway roundabout sediments



R1 - File: R1.RAW - Type: 2Th/Th locked - Start: 1.300 ° - End: 70.000 ° - Step: 0.020 ° - Step time: 2.4 s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 1.300 ° - Theta: 0.650 ° - Phi: 0.00 ° - Aux1: 0.0 - Au
Operations: Import