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ORIGINAL ARTICLE

Mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments, Cairns, northern Australia

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Abstract This investigation revealed the presence of traffic-derived metals within road, stream and estuarine sediments collected from a coastal catchment, northern Australia. Studied road sediments displayed variable total metal concentrations (median Cd, Cu, Pb, Pd, Pt, Ni and Zn values: 0.19, 42.6, 67.5, 0.064, 0.104, 36.7 and 698 mg/kg, respectively). The distinctly elevated Zn values are due to abundant tyre rubber shreds (as verified by SEM-EDS and correlation analysis). By comparison to the road sediments, background stream sediments taken upstream from roads have relatively low median Pb, Pd, Pt and Zn concentrations (7.3 mg/kg Pb, 0.01 mg/kg Pd, 0.012 mg/kg Pt, 62 mg/kg Zn). Stream and estuarine sediment samples collected below roads have median values of 21.8 mg/kg Pb, 0.014 mg/kg Pd, 0.021 mg/kg Pt and 71 mg/kg Zn, and exhibit ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios that appear on a mixing line between the isotopically distinct background stream sediments and the road sediments. Thus, mobilisation of dusts and sediments from road surfaces has resulted in relatively elevated Pb, Pd, Pt and Zn concentrations and non-radiogenic Pb isotope ratios in local coastal stream and estuarine sediments. The investigation demonstrates that traffic-derived metals enter coastal stream and estuary sediments at the fringe of the Great Barrier Reef lagoon.

Keywords Traffic pollution · Road sediments · Stream sediments · Metals · Pb isotopes · Australia

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Introduction

Road runoff water has been recognised as a major contributor to contamination problems in receiving water bodies (cf. Drapper et al. 2000; Toomey et al. 2003; Zhou et al. 2003). This is largely due to the fact that a significant amount of contaminants, ranging from gross pollutants to particulate, dissolved and soluble chemicals, accumulate on road pavements. The road runoff pollutants potentially impacting on sediment and water quality in receiving waters include dissolved and particulate trace metals (Sansalone and Buchberger 1997). The traffic-derived metals can be conveyed into the road drainage networks during runoff events (Rose et al. 2001). Unless treatment devices have been installed to remove trace metals from road runoff waters, the metals are transported into local stream systems, potentially interacting with ecosystems (cf. Forman and Alexander 1998) or accumulating in stream sediments (cf. Lee et al. 2003).

The concentration of metals in stream sediments is largely influenced by the parent materials, sediment type and anthropogenic additions. As a result, published total metal concentrations of contaminated and background stream sediments vary greatly, even on a local scale. Therefore, elemental concentration data on their own can be insensitive or unreliable indicators of anthropogenic influences in heterogeneous materials like stream sediments. In contrast, the use of Pb isotope data can resolve ambiguities where natural and anthropogenic sources of Pb cannot be easily distinguished solely based on concentration data. The technique is based on the fact that three of the four lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) are radiogenic and have increased in abundance as a function of the decay rate of their radioactive parent isotopes ^{238}U, ^{235}U, and ^{232}Th, respectively. In a closed system, the Pb isotope composition of a given sample depends on its age and U/Pb and Th/Pb ratios of the parent materials from which the Pb was derived (Gulson 1986). If there are additional anthropogenic contributors of Pb (i.e. vehicle exhaust) into the environment, this input commonly causes differences in Pb isotopic ratios in sediments (cf. Sutherland et al. 2003). Hence, variations in the Pb isotope ratios, such as ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb, are commonly used as tracers of environmental processes and as an indicator to differentiate the sources of Pb in environmental samples (cf. Gulson et al. 1994, 1995; Munksgaard et al. 2003).

To date, studies conducted on traffic-derived metals have focused on topsoils surrounding road corridors (cf. Piron-Frenet et al. 1994; Zupancic 1999; Turner and Maynard 2003). By comparison, the geochemistry of stream sediments impacted by road runoff waters remains largely unexplored and, there is little knowledge on the behaviour of trace metals in these environments (de-Vos et al. 2002). This paper reports on the chemical and physical characteristics of road sediments and on the mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments of the Avondale Creek catchment, north Queensland, Australia. Particular emphasis in this work is placed on trace metal and Pb isotope geochemistry as this has been used to identify traffic-derived metal impact in coastal stream and estuarine sediments.

Avondale Creek catchment

Physiography and climate

The Avondale Creek catchment is situated in the Wet Tropics Region of north Queensland, centred on 16°50′S, 145°40′E, approximately 15 km northwest of Cairns (Fig. 1). The catchment covers an area of ~30 km^2 and incorporates two prominent physiographic entities: the Barron-Atherton Tableland of undulating to hilly country to the west and the narrow Coastal Plain with flat to gently undulating lowlands to the east (Fig. 1). Altitudes in the catchment range from 0 to 610 mAHD. The north trending Great Dividing Range, a continental drainage divide, is located ~30 km to the west.

The region has a tropical monsoonal climate, with distinct wet and dry seasons and 80% of the annual rainfall occurring between November and April. The average annual rainfall in the region is at 2,000 mm (Cairns airport weather station, 7 km southeast of the catchment) (Bureau of Meteorology 2006). The relatively wet conditions are directly influenced by the proximity of the >600 m high escarpment to the west. The eastern margin of the rugged escarpment descends abruptly to the coastal plain, which is drained by Avondale Creek, associated tributaries and man-made drains, with drainage waters entering the Great Barrier Reef lagoon in the Coral Sea (Fig. 1).

Geology, soils and landuse

The upper Avondale Creek catchment consists of large tracts of Hodgkinson Formation, a regionally extensive Devonian succession comprised of turbiditic metasedimentary rocks, and minor late Permian Mt Formatine Granite (Willmott et al. 1988). The lower Avondale Creek catchment, including the Coastal Plain and the study area, consists of unconsolidated Quaternary colluvial, alluvial, coastal dune and estuarine deposits. Soils of the escarpment are red clay loams of metamorphic origin, and those of the lowlands formed on Quaternary alluvium comprise coarse sand and sandy loams (Murtha et al. 1996). The upper Avondale Creek catchment is completely forested and the area is included in the Wet Tropics World Heritage Area. The lowland country has been cleared for urban development and sugarcane production.

Roads

The Kuranda Range Road and the Captain Cook Highway are the major roads in the studied catchment (Fig. 1). The Kuranda Range Road accommodates an average daily traffic (ADT) volume of 6126 vehicles on two single lanes (Cherry 2005, personal communication). The course of the Kuranda Range Road between the coastal plain and the escarpment is convolute, includes 20 sharp bends and has an average grade of 6% (Cherry 2005, personal communication). The Captain Cook Highway comprises a dual carriage two-lane highway with several round-abouts, an ADT volume of 30,000 vehicles and a flat grade (Jones 2004, personal communication; Cherry 2006, personal communication). The highway surfaces comprise basalt aggregate

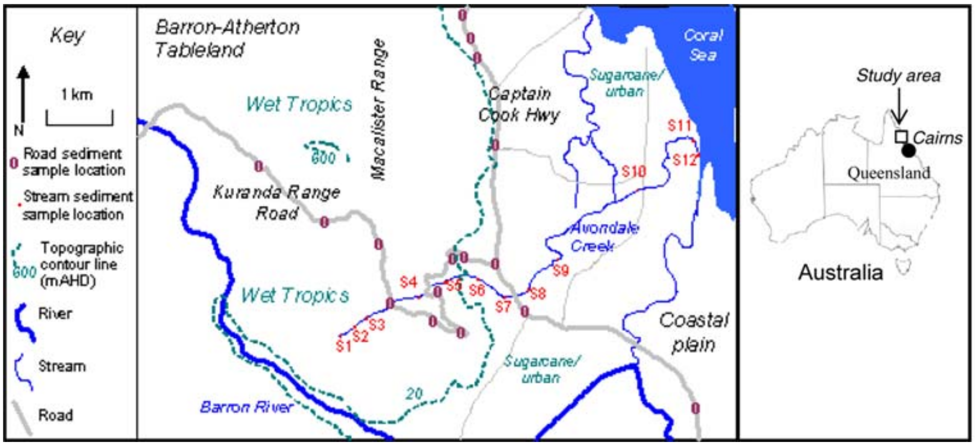


Fig. 1 Plan of the Avondale Creek catchment, north Queensland. Location of sample sites for road, stream and estuarine sediments, spot elevation, physiographic entities, and major landuses are indicated

and bitumen and, runoff waters from the Kuranda Range Road and Captain Cook Highway enter Avondale Creek via concrete gutters, swales and overland flows.

Materials and methods

Sampling and sample processing

Stream and road sediment samples were collected following prolonged dry periods from October 2002 to August 2004. Stream sediments (*n*: 12) were taken from Avondale Creek upstream from the Kuranda Range Road (samples S1–S3, representing local background), and downstream from the Kuranda Range Road and the Captain Cook Highway (samples S4–S12, representing traffic-impacted sediments) (Fig. 1). Stream sediments comprised composites taken from the top 5 cm of the active stream channel/estuary and constituted ~0.5 kg. Individual sediment samples were oven-dried (50°C) and sieved to less than 75 µm. In view of the abundance of coarse-grained rock particles in the headwaters of Avondale Creek and common geochemical stream sediment surveys (cf. Van Loon and Barefoot 1989), the fine-grained fraction of the sediments was selected as the fraction most likely to reflect hydromorphically dispersed metals and traffic pollution.

Road sediment samples were collected from the Kuranda Range Road (*n*: 30) and the Captain Cook Highway (*n*: 14) (Fig. 1). Road sediment was collected from each location on more than one occasion. The sediment was swept from road edges into a dustpan, taking care not to unsettle the fine dust component. Disturbance of this fine portion may result in its loss to the atmosphere (Serrano-Belles and Leharne 1997). Road sediment samples were sieved to less than 2 mm to include large (>1 mm) anthropogenic particles such as tyre rubber fragments, which are known to contain varying amounts of metals (Varrica et al. 2003).

Selected Avondale Creek sediments (*n*: 3) were investigated for their grain size distribution using a Malvern Mastersizer Laser Particle Size Analyser (JCU, Townsville). In addition, two composite road sediment samples were produced by mixing equal portions of individual road sediment samples (*n*: 6 from the Kuranda Range Road, *n*: 4 from the Captain Cook Highway). These two composite samples were analysed for their particle size distribution using a stack of ten brass sieves (aperture intervals: <38, 38–63, 63–75, 75–106, 106–250, 250–500, 500–1,000, 1,000–2,000, 2,000–4,000, >4,000 µm). Overall, ten sieved road sediment size fractions were obtained for analysis.

Analytical methods

Road, stream and estuarine sediment samples as well as the sieved road sediment size fractions were ground in a chrome-steel ringmill. Sample powders were dissolved in a hot HF–HNO_3–$HClO_4$ acid mixture and analysed by inductively coupled plasma atomic emission spectrometry (ICPAES) and inductively coupled plasma mass spectrometry (ICPMS) for their Cd, Cu, Pb, Ni and Zn contents at Australian Laboratory Services (ALS, Brisbane). Quality control/assurance of the data was applied using the repetitive processing of several aliquots of sample duplicates (*n*: 2), quartz blanks (*n*: 8) and the geochemical reference material GXR-3 (*n*: 7). Relative percent differences (RPDs) between elemental values detected in the parent and duplicate materials were nearly all (ca. 95% of values) within the ‘acceptable’ range, as stipulated by Australian Standards (1997). Maximum elemental concentrations detected in the quartz blank samples (Cd < 0.01 mg/kg, Cu 3.1 mg/kg, Pb 0.9 mg/kg, Ni

5 mg/kg, and Zn 4 mg/kg) were considerably lower than their respective minimum values detected in the studied road and stream sediments (refer to Table 1). Further to this, three of the quartz blank samples were passed through brass sieves and did not acquire any degree of metal contamination; hence rescinding the sieves as potential sources of metals to the sieved sediments. Deviations from the listed GXR-3 compilation values are for Cd, Cu, Pb, Ni and Zn generally less than 5%. In addition, selected road and stream sediment samples (n: 16) were submitted to the Advanced Analytical Centre (AAC, Townsville) for Fe and Mn analysis by X-ray fluorescence and to ALS for Pt and Pd analysis (n: 45) by nickel fire assays and ICPMS. Organic carbon (C_{org}) concentrations in road sediment size fractions (n: 9) and selected stream sediment samples (n: 3) were determined using a Leco furnace (ALS, Brisbane).

Elemental Pb and Pb isotope analyses were carried out on road and stream sediment samples using ICPMS techniques at the Australian Nuclear Science and Technology Organisation (ANSTO, Sydney). Samples were analysed for their $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios following digestion of the sediments in HF–HNO_3–HCl. Lead isotope analysis was performed using a quadropole ICPMS (Aligent 4500). Two stream sediment samples were duplicated for QA purposes and the RPDs between elemental values in the parent and duplicate samples were all within the 'acceptable' levels according to Australian Standards (1997).

Solid speciation of trace elements in road sediments can be evaluated using extraction techniques. The solubility of selected trace metals in Kuranda Range Road sediments was evaluated using two leaching methods. The oxide/oxyhydroxide fraction of the sediments was extracted by allowing two 1 g bulk road sediment samples (one from the Kuranda Range Road, and one from the Captain Cook Highway) to be leached in 50 ml of citrate-dithionate solution for 16 h at room temperature while undergoing constant agitation (Rayment and Higginson 1992). The experiment aimed to confirm that the oxide/oxyhydroxide fraction accommodated only minor amounts of trace metals in these sediments. Also, the bulk road sediment sample from the Kuranda Range Road was sequentially extracted. The procedure was designed to differentiate

Table 1 Elemental abundance within road, stream and estuarine sediments (<75 μm fraction), Avondale Creek catchment, north Queensland

	Cd	Cu	Pb	Ni	Zn	Pd	Pt	Fe (wt%)	Mn (wt%)	C_{org} (wt%)
Road sediments (n: 44)										
Minimum	0.05	19.2	11.8	24.5	112	0.001	0.0021	2.93	0.05	0.55
Maximum	1.22	179	976	94	3320	0.923	1.05	7.45	0.13	22.3
Arithmetic mean	0.22	48.6	115	39.7	960	0.123 (n: 38)	0.192 (n: 38)	4.41(n: 13)	0.068 (n: 13)	8.52 (n: 9)
Median	0.19	42.6	67.5	36.7	698	0.064	0.104	3.88	0.06	9.38
Standard deviation	0.17	27.73	155	14.1	797	0.187	0.219	1.21	0.024	7.6
Stream sediments; headwaters (background, n: 3)										
Minimum	0.11	25	7.2	42.1	51	0.0063	0.009			
Maximum	0.15	43.4	10.1	80.3	66	0.0131	0.014			
Arithmetic Mean	0.13	34.3	8.2	57.3	59.7	0.0097 (n: 2)	0.0115 (n: 2)	2.99 (n: 1)	0.06 (n: 1)	12.9 (n: 1)
Median	0.13	34.4	7.3	49.6	62	NA	NA			
Standard deviation	0.02	9.2	1.65	20.2	7.77	0.005	0.004			
Coastal stream sediments (n: 7)										
Minimum	0.03	28.7	17.2	19.2	60	0.009	0.0078	5.67 (n: 1)	0.13 (n: 1)	
Maximum	0.1	36.2	24	25.2	77	0.016	0.0126			
Arithmetic Mean	0.063	31.9	20.7	21.7	71.4	0.012 (n: 3)	0.0108 (n: 3)		3.5 (n: 1)	
Median	0.06	31.4	21.8	20.8	73	0.012	0.012			
Standard deviation	0.025	2.57	2.81	2.26	6.02	0.0035	0.0026			
Estuarine sediments										
S11	0.03	43.3	26.6	24.6	67	0.018	0.0166			
S12	0.07	20.2	29.6	23.9	298	0.01	0.0245	5.38	0.11	1.9 (n: 1)
ISQG values (NWQMS 2000)										
Low trigger values	1.5	65	50	21	200	NE	NE	NE	NE	NE
High trigger values	10	270	220	52	410	NE	NE	NE	NE	NE

Values in mg/kg unless otherwise stated

ISQG interim sediment quality guideline values (NWQMS 2000), *NE* none established among the water-soluble, exchangeable, carbonate, Fe–Mn oxyhydroxide, oxidisable (sulphides, organic matter), and residual element fractions (insoluble oxides, silicates). 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 extractants were analysed for Cd, Cu, Pb, Ni and Zn by ICPMS (AAC, Townsville). In addition, total metal contents were determined in order to calculate the amount of metals present in the residual solids from the sum of the eluates of the sequential extraction analysis. For this, three replicate samples of the bulk road sediment (<250 µm) were crushed to powder in a chrome steel ring mill, digested in HF–HNO_3–$HClO_4$ and analysed by ICPMS for their trace metal contents (ALS, Brisbane).

The mineralogy of road and stream sediments samples was identified using X-ray diffraction (Cu Kα; Siemens D5000 X-ray diffractometer) and computational software (EVA) (AAC, Cairns). Optical microscopy, scanning electron microscope (SEM) observations and semi-quantitative energy dispersive spectrometry (EDS) electron microprobe analyses were conducted on road sediments using a Jeol JSM-6300 with a Moran Scientific V8.5 Multi Channel Analyser (AAC, Cairns).

Results

Road sediments

The road sediments display major (i.e. >1 wt%) median concentrations of Fe and C_{org}, minor (i.e. >100 mg/kg) Mn, Pb and Zn, and traces (i.e. <100 mg/kg) of Cd, Cu, Ni, Pd and Pt (Table 1). Correlation analysis was performed on the road sediment elemental concentration data for the individual samples as well the sieved fractions. All values were log-normalised prior to the calculation of correlation coefficients. The analysis revealed the following significantly ($P < 0.05$) positive correlations: Cd–Zn, Cd–C_{org}, Cu–C_{org}, Pb–C_{org}, Ni–Fe, Zn–C_{org}, Pd–Pt, and Mn–Fe within the studied road sediments.

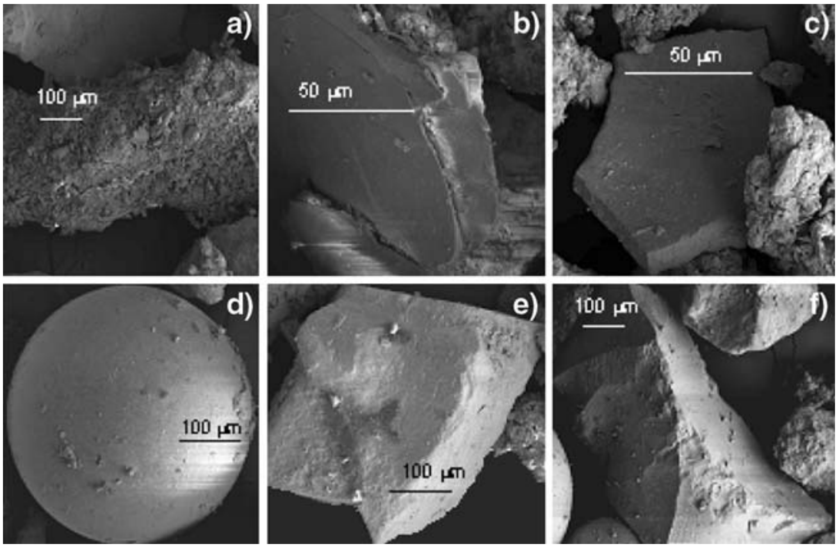
Total metal values in background stream sediments taken upstream of the Kuranda Range Road were compared with total road sediment metal values to estimate the degree of anthropogenic metal impact in the road sediments. The background stream sediment samples have relatively low trace metal concentrations with the exception of Ni (Table 1). By comparison, road sediments have distinctly elevated trace metal (Pb, Zn, Pd, Pt) contents. Compared with the mean values of background stream sediments, there has been moderate to strong enrichment of Pb, Zn, Pd and Pt of the road sediments (Table 1). Furthermore, median Ni, Pb and Zn values of road sediments exceed NWQMS (2000) sediment guideline values (ISQG-low) and thus, the sediments have to be regarded as contaminated.

The detected element distributions are consistent with the occurrence of relatively abundant mineral as well as anthropogenic particles, whose presence was verified by SEM analysis (Fig. 2). The road sediments are largely composed of coarse-grained (>100 µm in diameter) orthoclase, quartz, albite and muscovite as evidenced by XRD and SEM studies (Fig. 2). While the XRD analyses did not indicate any carbonates or organic matter, their presence is signified by detectable C_{carb} and C_{org} contents (Table 1). The road sediment particles range from coarse-grained, mineral fragments (>100 µm in diameter) to very fine, abraded metallic (Fe–Ti) particles (<10 µm in diameter) (Fig. 2). The sediment matrix is dominated by abundant tyre rubber shreds, which vary in length but commonly range between 100 and 250 µm in diameter (Fig. 2). SEM-EDS analysis showed that the surfaces of these rubber shreds are enriched with Zn.

Particle size analyses of road sediments demonstrate that the fine fraction (<106 µm) constitutes <10 wt% (Fig. 3a). Road sediment from the steep Kuranda Range Road is characterised by an abundance of coarse-grained particles (1,000–> 4,000 µm), whereas road sediment from the Captain Cook Highway has a much higher proportion of the medium-grained particle fraction (106–1,000 µm). Such distinctly different grain size distributions in the analysed road sediments are likely related to the difference in road grade. The gentle road surface of the Captain Cook Highway causes the increased capture of medium-grained sediments in road-side gutters, whereas the steeper Kuranda Range Road surface preferentially captures coarser-grained materials.

The chemical composition of the different size fractions of road sediment samples is heterogenous (Fig. 4), and the size fractions possess a range of element distributions: (1) the size fractions have minor (i.e. >100 mg/kg) median concentrations of Zn and traces (i.e. <100 mg/kg) of Cd, Cu, Pb and Ni; (2) Cd and Zn are concentrated in the medium-sized (106–250 µm) sediment fraction of the Kuranda Range

Fig. 2 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



Road; (3) Cd and Zn are most abundant in the fine-grained (<106 µm) sediment fraction of the Captain Cook Highway; (4) Cu and Pb concentrations increase with decreasing particle size in the Kuranda Range Road sediments; (5) Cu and Pb are concentrated in the medium- to fine-grained (<250 µm) sediment fraction of the Captain Cook Highway; and (6) Ni is concentrated in both, the coarse-grained and the fine-grained sediment fraction of the Kuranda Range Road and Captain Cook Highway. Consequently, large quantities of Cd, Cu, Pb and Zn are bound to the fine-grained (<250 µm) sediment fraction, whereas Ni is accounted for by fine- and coarse-grained particles.

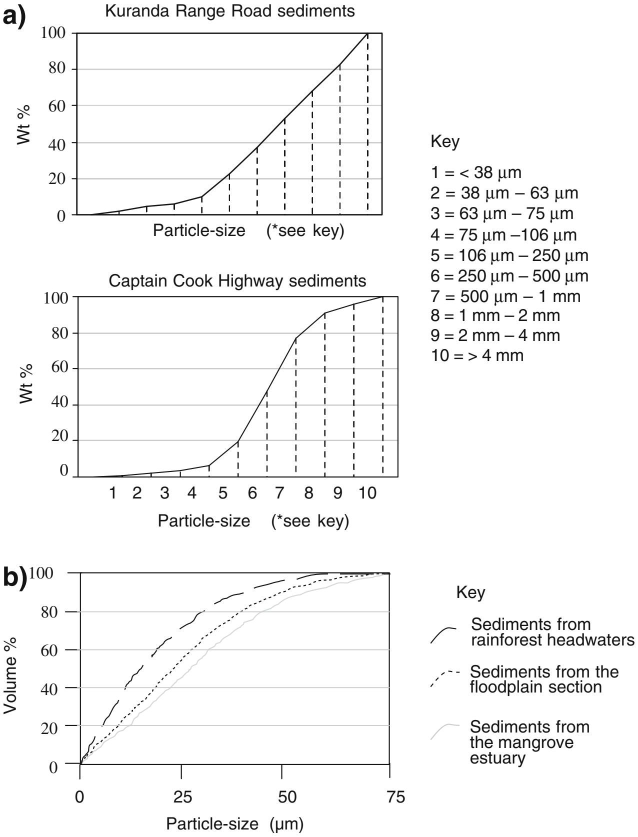


Fig. 3 Particle-size distributions of studied **a** road and **b** stream sediments

Characterisation of solid metal species in the Kuranda Range Road sediment was made by partial leach and sequential extraction procedures. Results show that Cd, Cu, Ni and Pb are present in the exchangeable, carbonate, oxidisable and residual sediment fractions, whereas Zn is also present in the Fe oxide/oxyhydroxide fraction and could not be detected in the oxidisable fraction (Fig. 5a, b). For Cu, Ni, Pb and Zn, the dominant transporting phase is the residual fraction, yet for Cd both the residual and oxidisable particulate forms are important. The water-soluble and exchangeable fractions carry Cd, Cu, Ni, Pb and Zn to a small extent. Abundant tyre particles are present in road sediments (Fig. 2) and therefore, much of the Zn would be expected to occur in the organic/sulphide fraction. Yet, the applied sequential extraction step yielded insignificant Zn proportions for this fraction. Thus, it appears that the oxidising agent applied in the sequential extraction scheme (HNO_3–H_2O_2) did not result in the dissolution of tyre particles.

Stream and estuarine sediments

Stream sediments in the studied Avondale Creek system vary from immature materials (gravel to cobble size) in the headwaters, through to sands, silts and

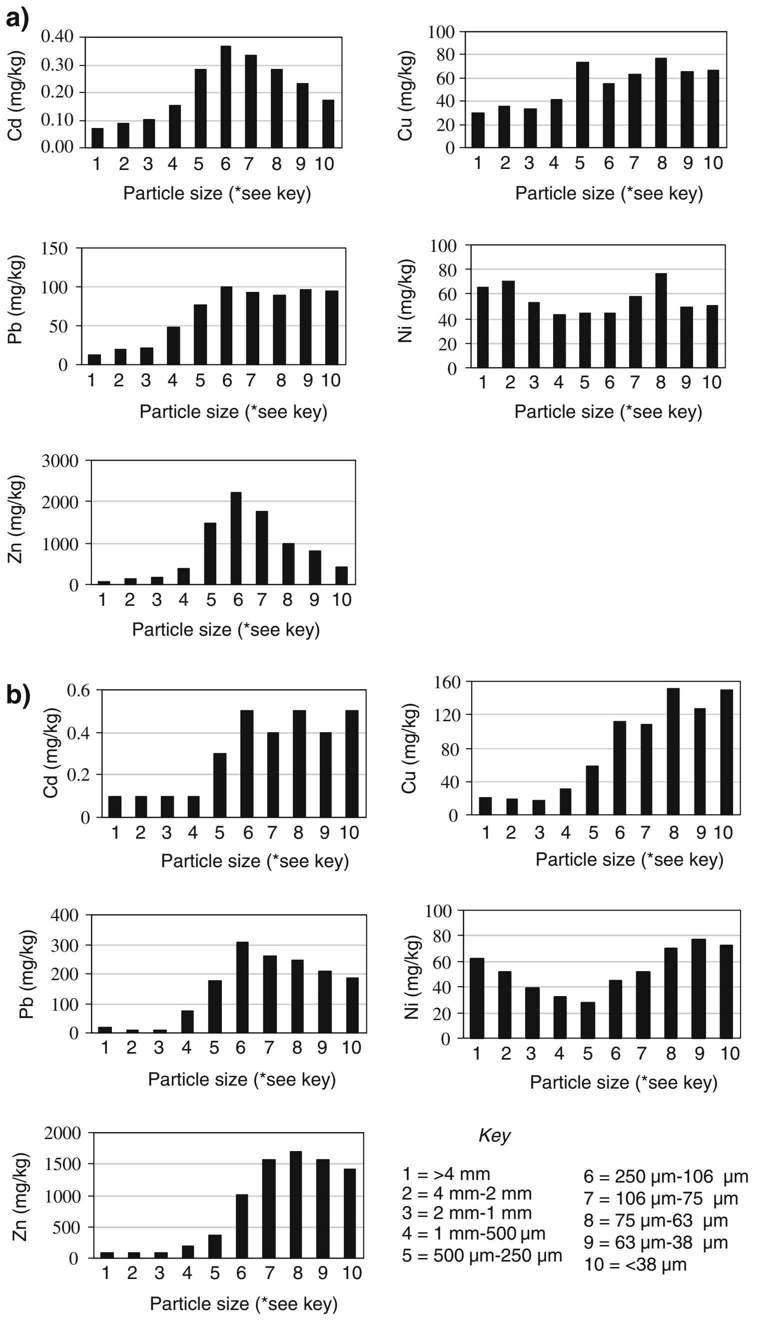


Fig. 4 Metal concentrations (Cd, Cu, Pb, Ni, Zn) of size fractions, Kuranda Range (**a**) and Captain Cook Highway (**b**) road sediments

muds deposited in low-energy settings of the coastal plain and estuary. Particle size analyses of the 75 μm stream sediment fractions demonstrate that ~50 vol% of stream sediments from the headwaters has a grain size of < 25 μm, whereas the 50 vol% of coastal and estuarine sediments have a grain size of < 15 μm and < 20 μm, respectively (Fig. 3b). Thus, coastal stream sediments have the greatest amount of fine-grained sediment particles. The sediments are dominantly composed of metasediment-derived detrital quartz and feldspars.

The geochemistry of Avondale Creek sediments is presented in Table 1. Organic material is particularly abundant in the rainforest headwaters (12.9 wt% C_{org}), whereas Fe and Mn oxides and oxyhydroxides are concentrated in the coastal stream and estuarine sediments as shown by elevated Fe and Mn values (Table 1). Sediments collected from headwaters and above the crossing with the Kuranda Range Road are considered to represent local background samples and, their fine fraction (<75 μm) has a mean Cd, Cu, Pb, Ni, Zn, Pd and Pt content of 0.13, 34, 8.2, 57, 59,

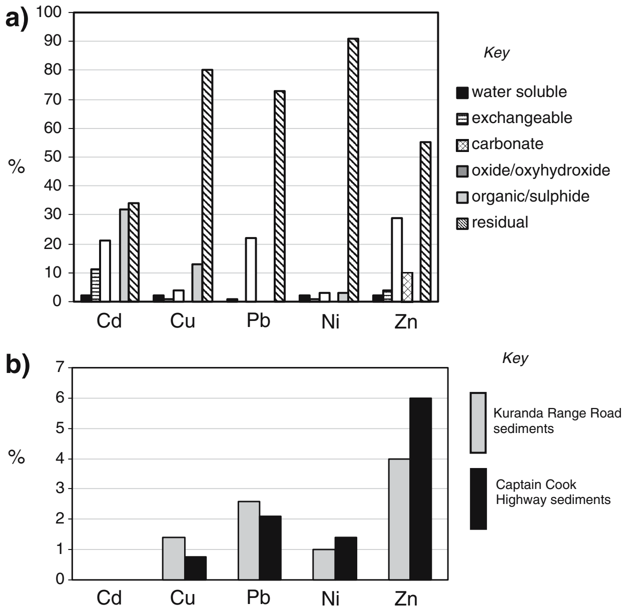


Fig. 5 **a** Calculated proportions of metals in road sediments subjected to sequential extraction. **b** Calculated proportions of metals in road sediments subjected to a partial citrate-dithionite extraction. For both extractions, the concentrations of the fractions have been averaged for all samples (*n*: 4) and calculated as a percentage of the total

0.009 and 0.011 mg/kg, respectively (Table 1). The mean Ni value exceeds the NWQMS (2000) sediment guideline value (ISQG-high). The elevated Ni concentration is likely the result of soil development over Ni-rich bedrock (i.e. basic volcanics within the Hodgkinson Formation), enrichment of relatively immobile elements (Ni) in the residual soil profile and transport of these Ni-rich soil particles into local streams.

The chemical composition of Avondale Creek sediments changes markedly below the Kuranda Range Road. Stream sediment samples taken downstream of the road display distinctly higher Pb, Pd and Pt than background sediments, with maxima in the downstream particulate Pb, Pd and Pt concentration profiles occurring in the estuary of Avondale Creek (Table 1; Fig. 6). In particular, there is a distinct enrichment of Pb (2×) in stream sediments compared with the mean values of background stream sediments (Table 1). By contrast, Cd and Ni are distinctly elevated in background samples compared to coastal and estuarine sediments, while stream sediments collected up to about 5 km downstream from the headwaters retain elevated Cu contents (Fig. 6). Although, the Zn concentrations of the < 75 μm coastal sediment fractions do not differ markedly from those of background samples, one sample taken from the estuary has a distinct Zn enrichment (4×) compared to all other samples (Fig. 6). None of the analysed stream and estuarine sediment samples possess chemical compositions that exceed the NWQMS (2000) sediment guideline values.

Lead isotope analyses reveal that the road and stream sediments possess distinctly different $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 7). The narrow range of the Pb isotope data for the background stream sediments indicates that the sediments had been weathered from source rocks of uniform isotopic composition. However, the coastal and estuarine stream sediments display slightly different $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 7). Several trends have been recognised within the data: (1) road sediments have the highest and least radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios; (2) coastal and estuarine stream sediments tend to have slightly higher Pb isotope ratios than the background sediments, with their ratios trending towards the less radiogenic ratios of road sediments (that is higher in $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios); and (3) the Pb isotopic ratios of the coastal and estuarine sediments relate to the total elemental Pb concentrations and there is significant positive correlation between the Pb isotope ratios ($^{208}\text{Pb}/^{206}\text{Pb}$) and the total Pb concentrations (correlation coefficient: $r^2 = 0.74$; $P < 0.05$).

Discussion

Road sediments as sources of trace metal contaminants

Road sediments are loose solids that settle and accumulate on road edges. These solids commonly consist of: (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 (cf. Sansalone and Buchberger 1997; Turner et al. 2001; Varrica et al. 2003). The combustion of fossil fuels (Pb) and the wear of catalysts (Pt, Pd), brake linings (Cu, Ni), tyres (Zn, Cd) and engines (Fe, Mn, Cr) in motor vehicles as well as the erosion and surface degradation of road pavements (Fe, Ni, V, Mg, Ca) and road signage and railings (Zn) lead to the release of metals and their accumulation in road sediments (Viklander 1998; Al-Chalabi and Hawker 2000). Road sediments thereby constitute the most immediate environmental sink for traffic-derived contaminants, and hence significant amounts of contaminants,

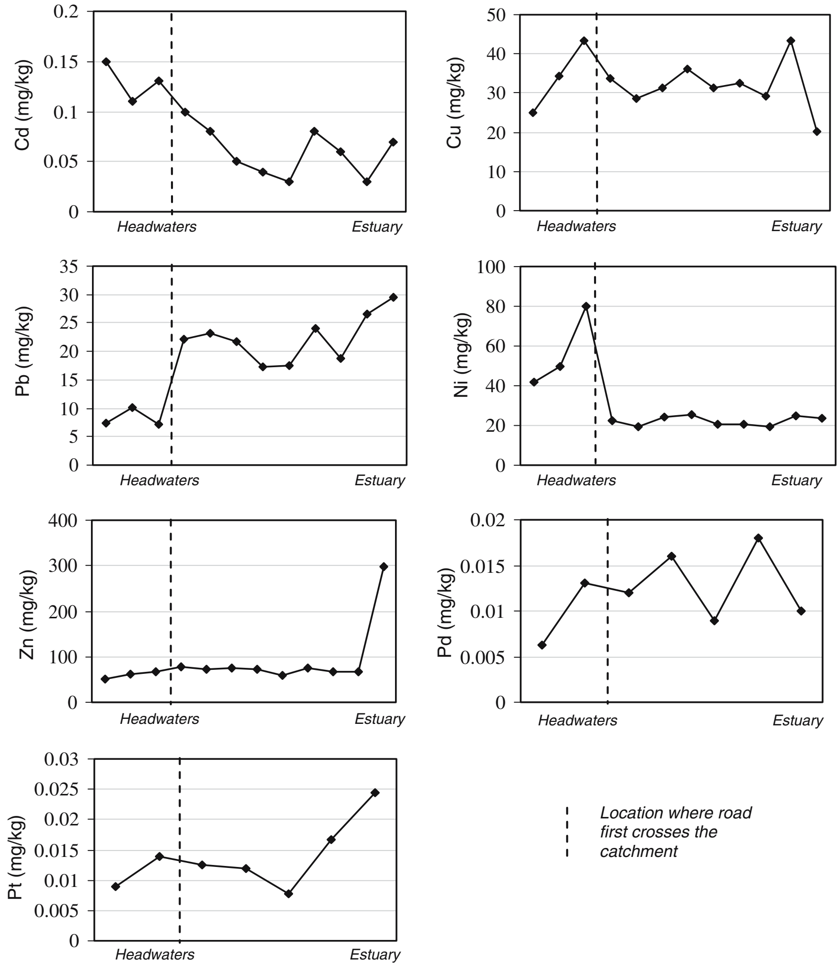


Fig. 6 Metal values (mg/kg) in stream sediments (<75 μm) from the Avondale Creek catchment. Samples are plotted so that the distance from the headwaters increases from left to right in a downstream direction

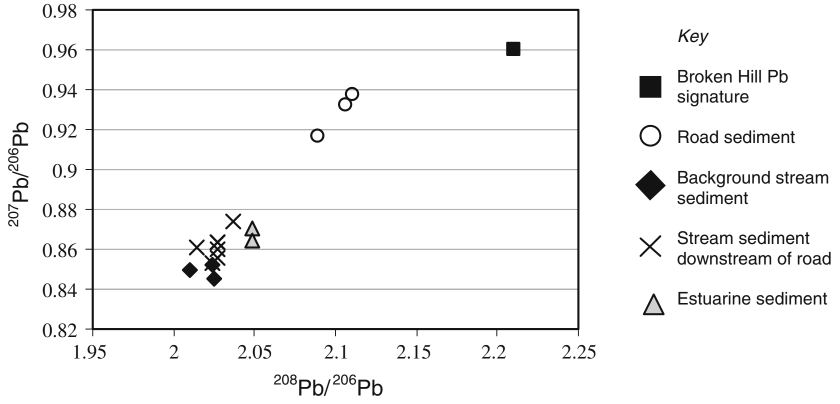


Fig. 7 Relationship between $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios for sediment samples (i.e. road, stream and estuarine sediment) from the Avondale Creek catchment. The Pb isotope composition of leaded fuel is also shown (Gulson et al. 1994, 1995)

ranging from gross pollutants to particulate, dissolved and soluble chemicals, accumulate on road surfaces and in gutters.

Previous research has documented that trace metals are generally concentrated in the fine-grained fraction (<75 μm) of road sediments (Viklander 1998; Birch and Scollen 2003; Varrica et al. 2003). In this study, most trace metals are concentrated in the <250 μm size fraction, reflecting the abundance of medium-grained Zn-rich tyre rubber shreds as evidenced by SEM studies (Fig. 2) as well as the significantly positive ($P < 0.05$) Zn–C_{org} correlation. The dominance of medium-grained tyre particles in road sediments of the Kuranda Range Road is likely due to the steep road gradient and numerous sharp bends leading to excessive tyre wear.

The application of the sequential and partial extraction reagents to the road sediments did not result in the dissolution of tyre particles. It appears that the HNO_3–H_2O_2 solution did not oxidise the rubber particles in the sample matrix and as a result, much of the Zn reported into the residual sediment fraction. Thus, the metal siting in road sediments should be further established using a combination of chemical extractions, elemental correlation analysis and microscopy investigations. The correlation analysis revealed significant ($P < 0.05$) positive relationships between trace metal values and C_{org} values, indicating an organic host for the metals; most likely tyre rubber shreds, whose abundance in the road sediment matrix was verified by SEM observations. In contrast, insignificant correlations between trace metal and Fe–Mn oxide values in the road sediment testify against the oxide/oxyhydroxide fraction as an important host for the studied trace metals. This finding is supported by the results of the sequential and partial extractions.

Overall, determination of trace metal siting in the studied road sediments reveals that a considerable portion of these contaminants may be mobilised from road surfaces into adjoining environments. Metals carried by tyre shreds can be physically deposited into roadside streams by gravity, wind or rain (cf. Sansalone and Buchberger 1997). Additionally, some of the trace metals contained in the road sediments may be soluble during rainfall and road runoff events. The sequential extraction analyses demonstrated that substantial proportions of Cd, Pb and Zn (20–30%) are present in the carbonate fraction (Fig. 5a). These metal fractions may be dissolved in slightly acid rainwaters (cf. Serrano-Belles and Leharne 1997). Such temporarily contained metal proportions may be liberated upon rainfall events into road runoff waters and discharged as dissolved species into local streams.

Dispersion into stream sediments

The chemistry of stream sediment is a function of the flux and chemical characteristics of detritus from the watershed to the depositional site and the proportions of inorganic and organic material incorporated into the sediment. In addition, natural geochemical cycles can be influenced by the addition of elements or compounds originating from anthropogenic activities.

Elevated Ni concentrations have been detected in background stream sediments of upper Avondale Creek which has a catchment containing basaltic rocks. Regions further downstream dominated by Quaternary sediments and flood plains have sediments with distinctly lower Ni concentrations. Such markedly different Ni distributions are likely the result of downstream dilution of Ni-bearing sediment particles. Thus, the Ni geochemistry of Avondale Creek sediments is largely controlled by the rock types present in the local catchment.

Stream sediments with distinctly elevated trace element (Pb, Pd, Pt, Zn) contents are located within the coastal and estuarine area. The spread of anthropogenic pollutants including Pb has been investigated by a number of studies. Investigations of Pb isotopic composition have thereby indicated that Pb pollutants are derived mainly from the combustion of Pb additives in petrol (cf. Gulson et al. 1981; Al-Chalabi and Hawker 2000). In Australia, accumulation of Pb has already been reported from surface soils adjacent to a number of major highways (cf. David and Williams 1975; Birch and Scollen 2003). Lead isotope analyses by this study have shown that the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the road sediments were extremely non-radiogenic compared to the stream and estuarine sediment samples, confirming the presence of anthropogenic Pb (Fig. 7). Thus, the observed Pb, Pd, Pt and Zn enrichment and the low $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios within coastal stream and estuarine sediments (Fig. 7) are likely caused by the transport of road sediments into the local drainage system and their dispersion into local creek and estuary sediments. Contamination of stream sediments by trace metals in the Avondale Creek catchment is evidently due to the transport of road sediments into the local stream system. The road surfaces act as line sources of trace metal contamination and affect the immediate area and the fluvial system downstream.

Overall, this research represents the first detailed study on metal ingress into streams from road sources. The presence of traffic-related metals in the studied stream and estuary has important environmental implications for all catchments affected by road runoff. Aquatic ecosystems are susceptible to metal contaminants mobilised by road runoff waters (e.g. Day et al. 1993; Sures et al. 2003; Wik and Dave 2005). 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). Additionally, the present study confirmed the presence of traffic-derived metal contaminants within the estuary of the Avondale Creek catchment, which feeds into the World Heritage-listed Great Barrier Reef. Hence, research into the bioavailability of traffic-derived metals in stream systems and on metal distributions in reef lagoonal sediments is recommended.

Conclusions

Road sediments from the Kuranda Range Road and Captain Cook Highway (Cairns, north Queensland) have distinctly elevated trace metal (Pb, Pd, Pt, Zn) concentrations, relative to background stream sediments. The elevated trace metal loads reflect the abundance of fine to medium-grained anthropogenic particles, including Zn-rich tyre rubber shreds and metal-rich shavings.

Total trace metal concentrations (Pb, Zn, Pt, Pd) of stream sediments generally increase downstream and below road crossings. The increase in trace metal concentration combined with a distinct change in the Pb isotope composition reflects the addition of anthropogenic trace metals. The elevated trace metal values are likely caused by abrasion of vehicle parts, vehicle emissions, and erosion and surface degradation of road infrastructure and paving materials and their subsequent transport by road runoff waters into the local drainage system.

This study has shown that contamination of stream sediments by trace metals in the Avondale Creek catchment is due to physical dispersion of road sediments into the local stream system. The road surfaces have acted as line sources of contamination and unconstrained drainage of road sediments occurs into the immediate area as well as the fluvial system downstream. Metal contaminants sequestered by coastal stream and estuarine sediments in the studied Avondale Creek catchment have the potential to be dispersed to the Great Barrier Reef Lagoon during cyclonic or flooding events.

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