

Trace metal enrichment in sugarcane soils due to the long-term application of fertilisers, North Queensland, Australia: geochemical and Pb, Sr, and U isotopic compositions

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Abstract. This study aimed to determine whether >80 years of fertiliser application has led to recognisable changes in the trace metal (Cd, Cu, Mo, Ni, Pb, Sr, Th, U, Zn) chemistry of topsoils (0–0.10 m) from sugarcane land, northern Queensland, Australia. The metal concentrations of commercial nitrogen (N) and potassium (K) fertilisers currently used in northern Queensland were generally lower than those of phosphate fertilisers and fertiliser blends. Composite topsoil samples (0–0.10 m depth) taken from canelands had higher median Cd, Mo, Pb, Sr, Th, U, and Zn concentrations than topsoils from forested areas of the catchment. Niobium, Ta, and Ti were confirmed as refractory immobile elements and used as reference elements for the evaluation of trace metal enrichments. Bivariate plots of trace metal/immobile element ratios verified that Cd, Mo, Pb, Sr, Th, U, and Zn are enriched in sugarcane soils compared with background forest soils. Isotopic ratios for Pb, Sr, and U highlight that fertilisers, cane soils, and forest soils have isotopically distinct compositions. Phosphate fertilisers currently used in the agricultural industry possess the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. Background forest soils have the highest $^{87}\text{Sr}/^{86}\text{Sr}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ and lowest $^{234}\text{U}/^{238}\text{U}$ ratios. By contrast, cane soils exhibit $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios that appear on a mixing line between the isotopically distinct background soils and phosphate fertilisers. Also, cane soils possess $^{234}\text{U}/^{238}\text{U}$ ratios similar to phosphate fertilisers. Thus, the application of phosphate fertilisers to canelands has resulted in higher Cd, Mo, Pb, Sr, Th, U, and Zn concentrations and more radiogenic Pb, Sr, and U isotope ratios in cane soils. Trace metal ratios and the Pb, Sr, and U isotopic composition of topsoils and fertilisers are useful tools to recognise fertiliser-derived trace metals in agricultural landscapes.

Additional keywords: fertiliser, trace metals, Pb isotopes, Sr isotopes, U isotopes, cane soils.

Introduction

The agricultural industry increasingly relies on manufactured fertilisers to provide nutrients to crops. Such practices cause the annual transfer of several hundred tonnes of metals and metalloids into soils globally because metals and metalloids are present as impurities and active compounds in agricultural chemicals (Nriagu and Pacyna 1988). The main source of fertiliser-derived contaminants in soils is phosphatic fertilisers, primarily due to impurities in the phosphate rock used for fertiliser manufacture (Williams and David 1973, 1976; Raven and Loeppert 1997; McBride and Spiers 2001). Much of the previous research has focused on the Cd content of fertilisers and their impact on agricultural soils (e.g. Williams and David 1973, 1976; McLaughlin *et al.* 2000; Taylor 1997). However, Molloy *et al.* (2005) concluded that other fertiliser-derived inorganic contaminants (specifically As, B, Cr, Cu, F, Hg, Ni, Pb, Se, and Zn) may also pose a particular environmental risk of accumulating in, or impacting on, soils, crops, and aquifers.

Topsoils used for sugarcane production in central and southern Queensland are known to possess elevated Cd and

Hg values compared with non-cane soils (Rayment *et al.* 1997). Such element enrichments have been assigned to the use of phosphate fertilisers and Hg fungicides. By comparison, the impact of fertilisers on the concentrations of other trace metals in cane soils remains relatively unexplored. This paper reports on metal distributions (Cd, Cu, Mo, Nb, Ni, Pb, Sr, Ta, Th, Ti, U, Zn) in cane soils of the Saltwater Creek catchment, North Queensland, Australia. Emphasis is placed in this work on trace element ratios and isotope studies as they have been used to identify fertiliser-derived trace metals in sugarcane lands.

Saltwater Creek catchment

Physiography and climate

The Saltwater Creek catchment is situated in the wet tropics region of North Queensland, centred on 16°24'S, 145°23'E, ~60 km north of Cairns (Fig. 1). The Saltwater Creek catchment covers an area of ~139 km². The catchment incorporates 2 prominent physiographic entities: the Palmer-Hodgkinson Uplands of deeply dissected, rugged mountainous country to the west, and the narrow Coastal Plain with flat to

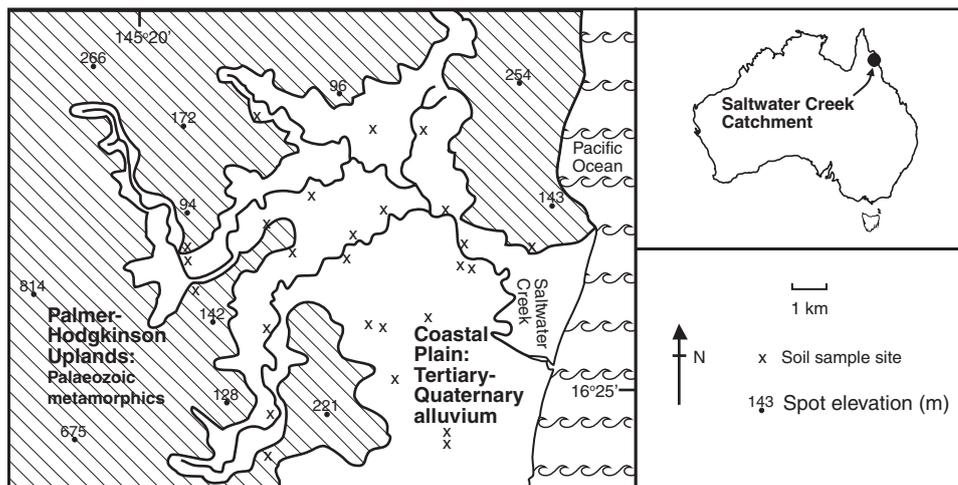


Fig. 1. Plan of the Saltwater Creek catchment, North Queensland. Location of sample sites for forest and cane soils, spot elevation, and physiographic entities are indicated.

gently undulating lowlands to the east (Fig. 1). Altitudes in the catchment range from 0 to 1300 m. The north-trending Great Dividing Range, a continental drainage divide (~1000–1300 m), is located ~10 km west.

The region has a tropical monsoonal climate, with distinct wet and dry seasons and 80% of annual rainfall falling between November and April. The average annual rainfall in the region has been estimated at 2003 mm (Port Douglas weather station, 10 km south-east of catchment) (Bureau of Meteorology 2008). The relatively wet conditions are directly influenced by the proximity of the up to 1300-m-high escarpment to the west. The eastern margin of the rugged Great Dividing Range descends abruptly to the coastal plain. The plain is drained by Saltwater Creek, associated tributaries, and man-made drains; drainage waters enter the Great Barrier Reef lagoon of the Pacific Ocean (Fig. 1).

Geology, soils, and landuse

The upper Saltwater Creek catchment (i.e. the Palmer-Hodgkinson Uplands) consists of large tracts of early Permian Mt Carbine Granite and Hodgkinson Formation, a regionally extensive Devonian succession comprising turbiditic metasedimentary rocks (Bultitude *et al.* 1996). The lower Saltwater Creek catchment (i.e. the Coastal Plain), including the study area, consists of partly consolidated Tertiary-Quaternary colluvial, alluvial, and coastal dune deposits and turbiditic metasedimentary rocks in the hills and slopes.

The upper catchment is covered with vine forest, and large areas of the forested lowland country have been cleared for agricultural production. The coastal lowlands are mainly utilised for sugarcane and to a lesser degree for cattle grazing and small-scale horticulture. Much of the agricultural land is found on Tertiary-Quaternary poorly sorted alluvial sands that derived from the weathering and erosion of the surrounding metamorphic rocks (Murtha 1989).

Soils used for agriculture on the coastal lowlands are largely poorly and well-drained soils formed on alluvium, and topsoils vary in texture from light-medium clays to sandy-silty loams

(Murtha 1989). Soils in the adjacent uncleared rainforest are dominantly red podzolic clay loams. The soils are naturally deficient in the major elements (N, P, K). Addition of these nutrients has been necessary for large-scale crop production in the form of fertilisers, particularly sugarcane since the 1920s (Pulsford 1993). In the Saltwater Creek catchment, N rates on cane were <100 kg/ha until the mid-1950s (Pulsford 1993). Rates increased during the 1960s and 1970s, with application of ~170 kg N/ha on plant cane and 180 kg N/ha on ratoons. Usage of P was at a low level, <10 t annually, prior to 1950 (Pulsford 1993). During the 1960s and 1970s, there has been an increase, generally in line with the area of sugarcane, reaching ~120 t P in 1981, with stability or a slight decrease in recent years. Usage in plant cane is ~60 kg P/ha, about 3 times the rate used on ratoons. Some ratoons may not be fertilised with P every year, so that the average rate for the whole cane area grown is 18 kg P/ha (Pulsford 1993).

Materials and methods

A suite of dry commercial fertiliser samples (12 different products including N, P, K, and blended fertilisers) was obtained from the Queensland Department of Natural Resources and Water, Mareeba. This suite is representative of fertilisers currently being used in the agricultural industry of North Queensland. In addition, bagged phosphate fertilisers were purchased from a local supplier in Mossman (6 km south of the catchment). Several hundred grams of dry commercial phosphate fertilisers (3 different products including superphosphate, diammonium phosphate, and N-P-K fertiliser blend) used in the cane industry were taken from the bags using a plastic scoop. Representative subsamples were ground to powders using a chrome-steel ring mill, and a 2-g sample was dissolved in 30 mL aqua regia for 20 min at room temperature. Sample solutions were subsequently analysed by inductively coupled plasma mass spectrometry (ICPMS) for Ag, As, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Sr, Th, Tl, U, and Zn at the James Cook University Advanced Analytical Centre (JCU AAC, Townsville).

In all, 27 soil sampling sites were chosen in the lower Saltwater Creek catchment to give a sampling grid of ~1 sample per 4 km². Soil samples were taken from 2 environments: (1) sugarcane land ($n=19$), and (2) forested areas that have never been cleared for agricultural production ($n=8$). Topsoil samples were taken using a plastic trowel (depth 0–0.10 m; ~1 kg). Each sample consisted of 5–10 subsamples taken from a 4-m² area, and these subsamples were composited to improve site representativeness.

Soil sample powders were fused with lithium metaborate and dissolved beads analysed for their total trace metal (Ag, Cu, Mo, Ni, Pb, Sr, Ta, Th, Tl, U, Zn, Zr) content by ICPMS at Australian Laboratory Services (ALS, Brisbane). Sample powders were also dissolved in strong acids (HF, HNO₃, HClO₄) and analysed for Cd by ICPMS at ALS. In addition, representative aliquots of soil samples were analysed by X-ray fluorescence for Ti and Nb (JCU AAC). Quality control/assurance of the data was obtained using analyses of sample replicates, blanks, and international reference standard GXR-3. The obtained GXR-3 concentrations corresponded closely to the published compilation concentrations with the exception of Zr concentrations, most likely due to incomplete digestion of zircon phases. Standard deviation values for the repeated analysis of the reference material were <5% of the mean concentrations for each element, indicating high accuracy of the results.

The Pb isotope ratios in topsoils ($n=27$) and selected phosphate fertilisers ($n=5$) were evaluated using a 1 M HCl partial extraction technique. The extraction procedure was chosen to yield dilute-acid extractable Pb isotope ratios because: (a) the use of 1 M HCl soluble metal concentrations as an estimate of the maximum bioavailable fraction has been recommended by the Australian and New Zealand Environment and Conservation Council (ANZECC 2000); (b) fertilisers are readily soluble in soil environments and hence a mild acid leachate was applied to target the soluble Pb isotope fraction in the investigated soils; and (c) since a considerable fraction of the total Pb is likely tightly bound in mineral particles and a dilute acid extraction will not remove the mineralised fractions, analysis of the dilute-acid extractable Pb isotope ratios would provide more appropriate data for recognising fertiliser impacts on soils. Approximately 0.5 g of sample was extracted in 5 mL 1 M HCl at 30°C for 1 h. Lead isotope analyses of the leachates were carried out using ICPMS techniques (quadropole ICPMS ELAN 6000) at Charles Darwin University (Darwin). Quality control/assurance of the partial extraction data was applied using subsample duplicates, digest blanks, and geochemical reference materials (AGAL-12, IAEA-Soil 7). The determined Pb isotope ratios carried precisions on XXX/206 (where XXX=207 and 208) ratios of ~0.5%. The Pb isotope ratios ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb were measured by normalising to the NIST-SRM981 Standard Reference Material (²⁰⁷Pb/²⁰⁶Pb=0.91464 and ²⁰⁸Pb/²⁰⁶Pb=2.1681).

Exploratory Sr isotope (⁸⁷Sr/⁸⁶Sr) analyses were conducted on 1 M HCl leachates of selected topsoils ($n=7$) and phosphate fertilisers ($n=3$). Approximately 0.5 g of sample was leached in 5 mL 1 M HCl at 20°C for 1 h. Strontium in the samples was purified using nitric acid and column chromatography with an Eichrom Technologies cation exchange resin. ⁸⁷Sr/⁸⁶Sr values

were measured on a VG Sector 54 Thermal Ionisation Mass Spectrometer at CSIRO Petroleum Resources (Sydney, Australia). These analyses carried precisions of 10–18 ppm (2σ). All ⁸⁷Sr/⁸⁶Sr data were normalised to the NIST-SRM987 value of 0.710240 (Hart *et al.* 2004).

Exploratory U isotope (²³⁴U/²³⁸U) analyses were conducted on selected topsoils ($n=7$) and phosphate fertilisers ($n=2$) at the Institute for Environmental Research (ANSTO, Sydney). Approximately 5 g of each sample was brought into complete dissolution using repeated acid attacks with HF, H₂O₂, HClO₄, HNO₃, and HCl. The solution was heated to dryness and the residue dissolved in 6 M HCl. Uranium was co-precipitated with Fe, Fe was extracted with ether, and U was separated by ion exchange resins from other elements. Uranium was electro-deposited on a stainless-steel disk. The U isotope composition (²³⁴U/²³⁸U) was determined on each stainless steel disk using α spectrometry and counting for 1–5 days depending of the activities of the radionuclides. The activity ratio (AR) was calculated from the activities of ²³⁴U and ²³⁸U. The analyses carried precisions of ~300–500 ppm.

Results

Fertilisers

The Ag, As, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Sr, Th, Tl, U, and Zn contents of K and N fertilisers are generally low, with the fertilisers having total As, Cd, Cu, Ni, Pb, Tl, U, and Zn below detection limits (Table 1). By contrast, the phosphate fertilisers and the trace metal enriched phosphate blends contained detectable concentrations of Ag, As, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Sr, Th, Tl, U, and Zn (Table 1). Such a relative metal enrichment of phosphate fertilisers and trace metal enriched phosphate blends is commensurate with the known metal chemistry of commercial fertilisers (McBride and Spiers 2001). The isotope analyses reveal that the phosphate fertilisers have the lowest and most radiogenic ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁶Pb, and ²⁰⁸Pb/²⁰⁶Pb ratios of all analysed samples (Tables 1, 2). Furthermore, the ²³⁴U/²³⁸U ratio of phosphate fertilisers is near unity, reflecting an abundance of radiogenic ²³⁴U. The distinctly radiogenic Sr and Pb isotope signature of phosphate fertilisers is likely caused by their elevated Rb and U contents.

Topsoil chemistry

A summary of the trace metal chemistry of topsoils from the Saltwater Creek catchment is given in Table 2. A comparison of trace metal concentrations within the cane and forest soils has been based on: (a) the mean metal concentration plus 1 standard deviation; and (b) the median metal value. The mean Cd, Mo, Pb, Sr, Th, U, and Zn content plus 1 standard deviation and the median Cd, Mo, Pb, Sr, Th, U, and Zn value are distinctly higher in the cane soils than in the forest soils (Table 2).

The level of metal accumulation in soils is largely influenced by underlying parent materials, soil type, and anthropogenic additions. Thus, published total metal concentrations of soils vary greatly, even on a local scale, and elemental concentration data on their own can be insensitive indicators of anthropogenic influences in heterogeneous environments such as soils. A more reliable determination of natural levels of metals is best done on the basis of immobile elements and trace element ratios.

Table 1. Trace metal and isotope (Pb, Sr, U) chemistry of commercial fertilisers (N-P-K) used in the agricultural industry, North Queensland
 Elemental analyses of the same fertiliser types have been averaged and the number of samples indicated (*n*). The fertilisers are listed with their N-P-K percentages. All values are given in mg/kg dry weight. All fertiliser samples possess <0.5 mg/kg of Hg. Plus: fertiliser blends with added trace metals; ^{207/206}Pb, ^{208/206}Pb, and ^{87/86}Sr isotope ratios in the 1 M HCl soluble fraction; ^{234/238}U in the total sample. DAP, Di-ammonium phosphate; SP, superphosphate; TSP, triple SP; LOD, limit of detection; MKP, potassium di-hydrogen orthophosphate

Fertiliser type (N-P-K)	Ag	As	Cd	Cu	Mo	Ni	Pb	Sb	Sr	Th	Tl	U	Zn	^{207/206} Pb	^{208/206} Pb	^{87/86} Sr	^{234/238} U
LOD	<0.05	<1	<0.05	<0.1	<0.03	<0.1	<0.05	<0.05	<0.03	<0.05	<0.05	<0.05	<5				
Urea, 41-0-0 (<i>n</i> = 2)	<0.05	<1	<0.05	<0.1	<0.03	<0.1	<0.05	<0.05	0.55	<0.05	<0.05	<0.05	<5				
KCl, 0-0-50	0.05	<1	<0.05	<0.1	0.15	<0.1	<0.05	0.27	2.1	0.47	<0.05	<0.05	<5				
13-2-13	0.3	<1	0.85	50.4	0.89	35.5	<0.05	1.09	22.3	1.77	0.78	73.1	251				
14-15-13	0.11	<1	0.54	46.3	2.33	30.2	<0.05	1.25	6.67	1.68	0.52	63.1	212				
14-15-13 plus	0.09	1.9	0.89	45	6.46	29.5	1.03	1.85	4.42	1.49	0.36	64.9	8800				
13-14-12 plus	0.19	5.8	0.85	35.4	6.4	25.2	1.32	18	6.08	2.13	0.62	46.4	17 700				
12-13-18	<0.05	5.81	0.60	43.9	2.31	28	0.23	0.66	15.2	<0.05	0.26	<0.05	120	0.6573	1.5982	0.71417	
30-3-14	<0.05	<1	0.11	6.21	3.96	2.78	0.53	0.05	3.03	<0.05	0.05	5.97	27.8				
29-0-18	<0.05	<1	<0.05	1.22	5.68	2.07	2.78	0.33	19.8	<0.05	<0.05	<0.05	5.5				
DAP, 18-20-0 (<i>n</i> = 3)	4.44	5.43	1.18	55.9	3.48	23.5	0.33	0.77	4.43	0.88	0.29	21.5	165	0.6672	1.6107	0.70852	1.04
SP, 0-9-0 (<i>n</i> = 4)	3.18	2.46	22	11.2	4.18	16.6	5.43	1.06	295	1.48	<0.05	29.6	105	0.6394	1.5435	0.70901	0.99
TSP, 0-21-0	0.52	2	6.67	7.87	0.36	30	6.68	4.38	0.79	7.69	0.76	183	108				
MPK	<0.05	15	<0.05	<0.1	0.21	<0.1	<0.05	4.39	5.98	<0.05	<0.05	<0.05	<5				

Refractory trace elements in soils exhibit constant element ratios even when their total soil concentrations become enriched or depleted during pedogenesis. In strongly weathered tropical soils, Nb, Ta, and Ti have been established as immobile elements, displaying a restricted range of immobile element ratios (e.g. Kurtz *et al.* 2000; Meijer and Buurman 2003; Buurman *et al.* 2004). The recognition of immobile elements allows the determination of gains and losses of other elements, which can be established relative to the immobile elements. Consequently, metal-contaminated soils tend to have higher metal/immobile element ratios, reflecting the anthropogenic addition of metals. Such a normalisation procedure has the potential to separate natural background from contaminated soil populations.

In the soils studied, the Ti, Nb, and Ta concentrations display strong positive correlations (Ti–Nb +0.8, Ti–Ta +0.65, Nb–Ta +0.78), and both the cane and forest soils display a narrow range of Ta/Nb and Nb/Ti ratios (Fig. 2*a, b*). The fact that these ratios

Table 2. Trace metal and isotope (Pb, Sr, U) chemistry of cane and forest soils

Elemental values are given in mg/kg dry weight. All samples possess <1 mg/kg Ag and <0.5 mg/kg Tl. *n*, No. of samples. $^{207/206}\text{Pb}$, $^{208/206}\text{Pb}$, and $^{87/86}\text{Sr}$ isotope ratios in the 1 M HCl soluble fraction; $^{234/238}\text{U}$ in the total sample; LOD, limit of detection

	LOD	Min.	Max.	Mean	Median	s.d.
<i>Forest soils (n = 8)</i>						
Cd	0.02	<0.02	0.04	<0.02	<0.02	0.01
Cu	5	8	21	12.6	11.5	4.34
Mo	2	<2	6	2.5	2	1.41
Nb	2	9	26	16.4	15	7.11
Ni	5	<5	24	10.3	8.5	6.71
Pb	5	8	25	14.9	13	5.27
Sr	0.1	6.4	36.7	18.1	16.9	8.64
Ta	0.5	<0.5	1.4	0.83	0.85	0.31
Th	1	6	13	9.5	9.5	2.32
Ti	5	2690	6920	4210	4073	1417
U	0.5	1.3	2.3	1.83	2.0	0.45
Zn	5	28	41	34	33	4.50
$^{207/206}\text{Pb}$ (<i>n</i> = 8)		0.8300	0.8629	0.8427	0.8380	0.0120
$^{208/206}\text{Pb}$ (<i>n</i> = 8)		2.0785	2.1139	2.0980	2.1007	0.0138
$^{87/86}\text{Sr}$ (<i>n</i> = 3)		0.7181	0.7208	0.7191		
$^{234/238}\text{U}$ (<i>n</i> = 4)		0.83	1.00	0.92		
<i>Cane soils (n = 19)</i>						
Cd	0.02	0.03	0.15	0.07	0.06	0.04
Cu	5	5	21	10.4	9	3.71
Mo	2	<2	36	6.16	3	8.29
Nb	2	8	22	14.5	15	4.17
Ni	5	<5	21	9.11	7	5.21
Pb	5	10	37	25.3	28	8.79
Sr	0.1	10.5	44.7	25.7	29.1	9.97
Ta	0.5	<0.5	1.4	0.91	0.9	0.28
Th	1	6	39	21	22	10.5
Ti	5	2190	5130	3820	3860	776
U	0.5	1.3	6.3	3.7	3.3	1.37
Zn	5	31	75	49.5	46	13.3
$^{207/206}\text{Pb}$ (<i>n</i> = 19)		0.8192	0.8498	0.8305	0.8307	0.0069
$^{208/206}\text{Pb}$ (<i>n</i> = 19)		2.0540	2.1098	2.0739	2.0716	0.0134
$^{87/86}\text{Sr}$ (<i>n</i> = 4)		0.7112	0.7286	0.7171		
$^{234/238}\text{U}$ (<i>n</i> = 3)		1.00	1.03	1.01		

remain constant in forest and cane soils implies that Nb, Ta, and Ti behaved as immobile elements during pedogenesis and that the forest and cane soils derived from the same geological bedrock (i.e. metasediments exposed in the surrounding hills). The alternative explanation that the 3 elements were lost at the same rate at all sites is perceived as unlikely. The immobile element ratio approach has been used to determine the addition of trace metals to the studied soils. Niobium and Ti were considered as immobile elements, although normalising to Ta instead of Nb produces nearly identical results. The cane soils display distinctly higher Cd/Nb, Mo/Nb, Pb/Nb, Sr/Ti, Th/Nb, U/Nb, U/Ti, and Zn/Ti ratios than the forest soils (Fig. 3*a–e*). By contrast, forest and cane soils display a similar range of Cu/Nb and Ni/Ti ratios (Fig. 4). Thus, the Cu and Ni concentrations of cane soils do not appear to be enriched and these element contents represent natural local background values. By contrast, Cd, Mo, Pb, Sr, Th, U, and Zn are variably enriched

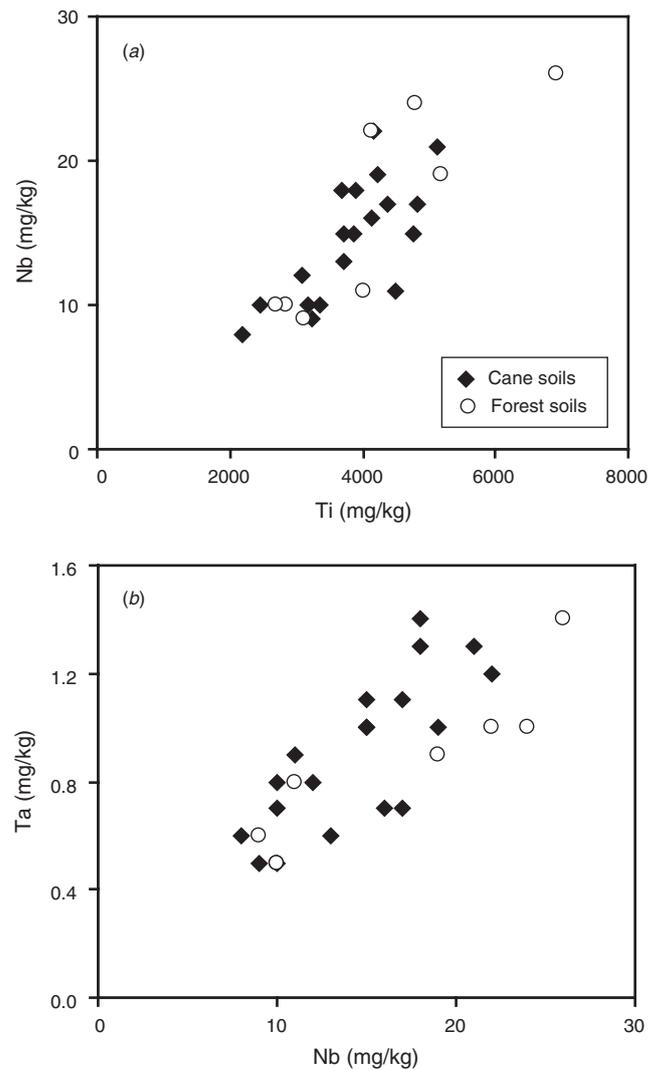


Fig. 2. Bivariate plots of element concentrations for cane and forest soils: (a) Ti v. Nb, (b) Nb v. Ta. Both soil types possess a restricted, yet similar, range of Nb/Ti and Ta/Nb ratios, demonstrating that the elements are immobile.

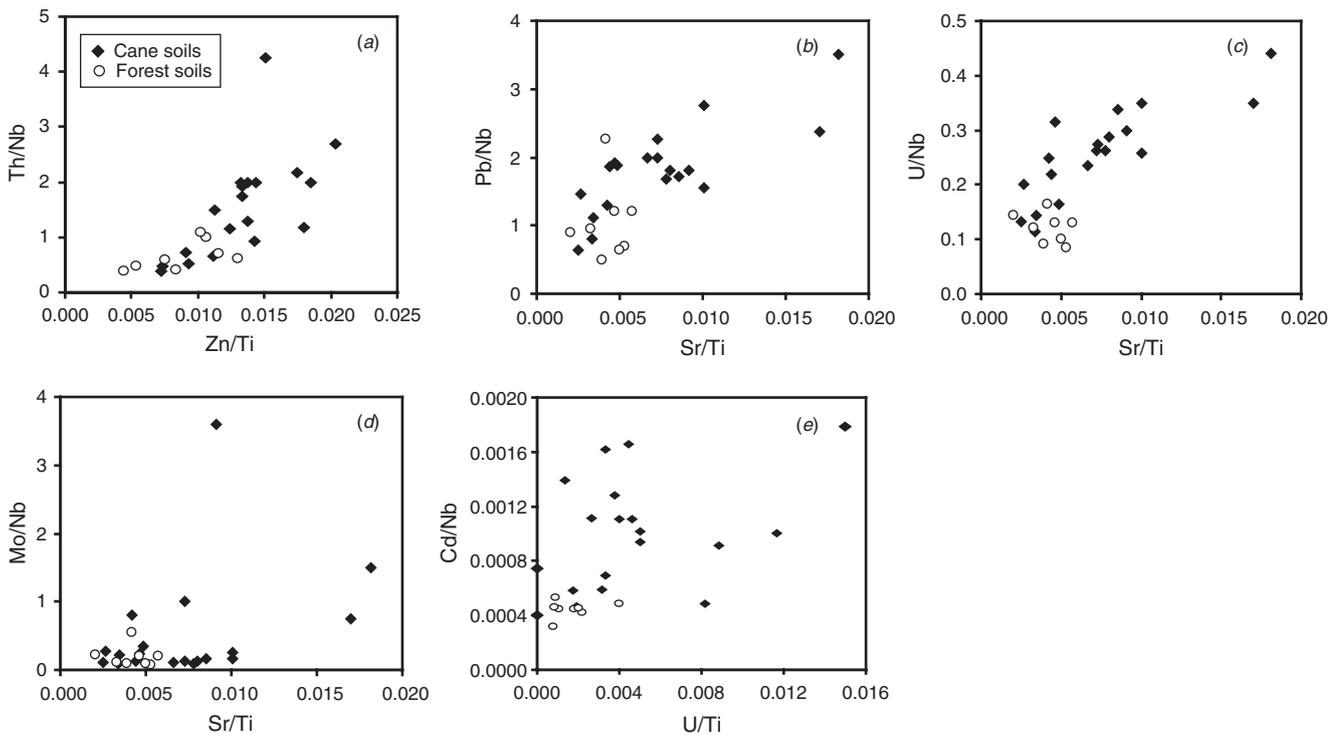


Fig. 3. Bivariate plots of element ratios for cane and forest soils: (a) Zn/Ti v. Th/Nb, (b) Sr/Ti v. Pb/Nb, (c) Sr/Ti v. U/Nb, (d) Sr/Ti v. Mo/Nb, (e) Cd/Nb v. U/Ti. Cane soils tend to possess higher element ratios than forest soils, illustrating the enrichment of Cd, Mo, Pb, Sr, Th, U, and Zn concentrations in cane soils.

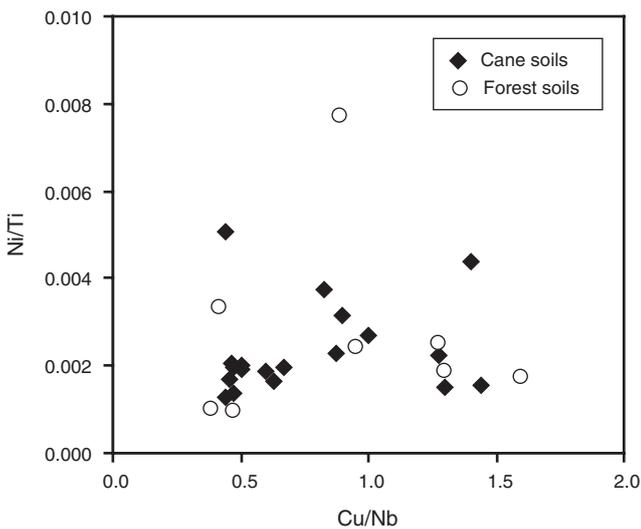


Fig. 4. Bivariate plot of Cu/Nb v. Ni/Ti for cane and forest soils.

in the cane soils relative to the forest soils unaffected by agricultural activities.

Isotope chemistry of soils

Isotope analyses of Pb, Sr, and U reveal that the cane and forest soils possess distinct $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{234}\text{U}/^{238}\text{U}$ ratios (Table 2). The 2 soil types display slightly different $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{234}\text{U}/^{238}\text{U}$

ratios (Table 2; Fig. 5a). Several trends have been recognised within the data: (1) background forest soils have the highest and least radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{234}\text{U}/^{238}\text{U}$ ratios (Table 2, Fig. 5b); (2) cane soils tend to have slightly lower Sr and Pb isotope ratios than the background soils, with their ratios trending towards the more radiogenic ratios of phosphate fertilisers (i.e. lower in $^{87}\text{Sr}/^{86}\text{Sr}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios) (Table 2, Fig. 5b); and (3) the $^{234}\text{U}/^{238}\text{U}$ ratios of cane soils are slightly higher than those of the background soils and identical to those of phosphate fertilisers (Table 1). However, the Pb isotopic ratios in 1 M HCl extracts of cane soils do not relate ($r = -0.64$) significantly to their total elemental Pb concentrations (Fig. 6). That is, the total Pb concentrations of cane soils only very slightly increase with decreasing Pb isotope ratios, trending towards the more radiogenic ratios of phosphate fertilisers. Such a minor shift in Pb isotope composition with Pb concentration suggests that fertiliser application has only a small impact on Pb soil chemistry.

Discussion

Origin of soil chemistry

The metal content of a soil is a function of natural geochemical concentrations and addition of elements or compounds originating from anthropogenic activities. Concentrations of Cd, Cu, Mo, Ni, Pb, Sr, Th, U, and Zn for soils have been stated as 1, 2–100, 2, 5–500, 2–200, 50–1000, 13, 1, and 10–300 mg/kg, respectively (Berkman 1976). Inevitably, most

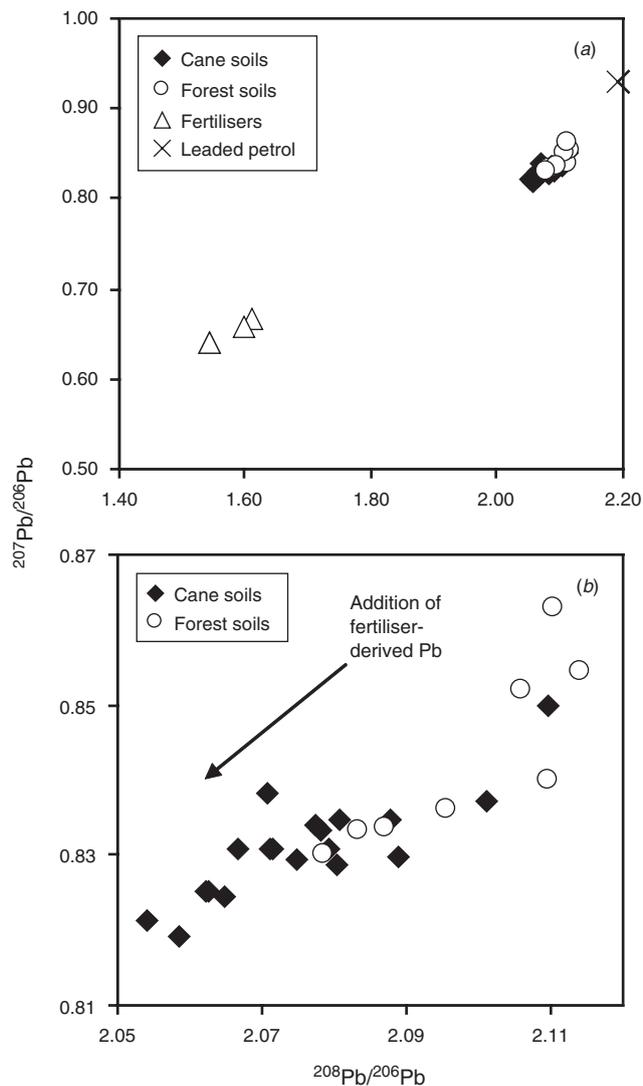


Fig. 5. Lead isotope ratios for 1 M HCl soil extracts. (a) Relationship between $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios for fertiliser and soil samples from the Saltwater Creek catchment. The Pb isotope composition of leaded fuel is also shown (Gulson *et al.* 1994). (b) Enlarged portion of Fig. 5a, showing that the cane soils tend to have lower $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than the forest soils due to the addition of fertiliser-derived Pb.

soil geochemical surveys include sites affected by atmospheric inputs (e.g. short-range and long-range atmospheric deposition of aerosols originating from waste incinerators, car exhausts, smelters, bushfires) or agricultural amendments (e.g. sewage sludges). Pristine background concentrations would be lower. In this study, the detected average Cu, Ni, Pb, and Zn values in the studied forest soils (12.2, 9.89, 16, and 35.1 mg/kg, respectively; Table 2) are similar to those of topsoils unaffected by agricultural activities and taken from National Park, State Forest, and bushland in southern Queensland (16, 6, 14, and 21 mg/kg, respectively) (Olszowy *et al.* 1995).

Elevated Cd and Hg values have been detected in cane soils of central and southern Queensland (Rayment *et al.* 1997). Such element enrichments have been assigned to the use of phosphate

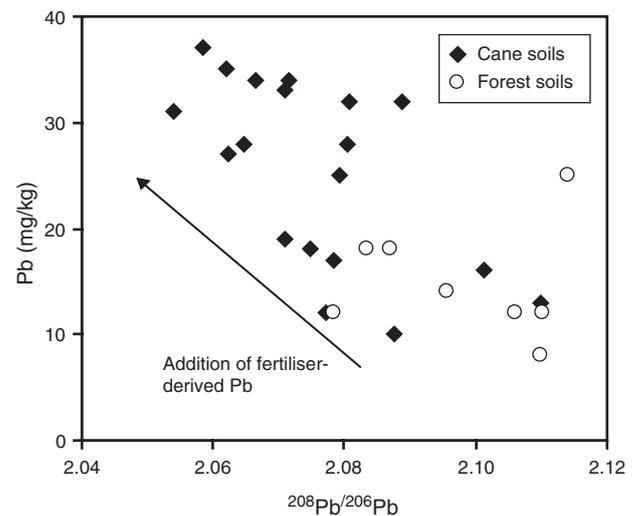


Fig. 6. $^{208}\text{Pb}/^{206}\text{Pb}$ for 1 M HCl soil extracts v. total Pb in cane and forest soils. Cane soils tend to possess higher total Pb and lower $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than the forest soils, caused by the admixing of fertiliser-derived Pb to cane soils.

fertilisers and Hg fungicides. Yet, the Cd, Pb, and Zn concentrations for cane soils of northern New South Wales were similar to or even lower than those in non-cane soils (Rayment *et al.* 1998). Thus, the use of metal concentration data on their own did not allow the recognition of anthropogenic-derived metals in cane soils.

Analyses of topsoil samples from canelands by this study have revealed Cd, Cu, Mo, Ni, Pb, Sr, Th, U, and Zn concentrations that fall into established background concentrations of soils (Berkman 1976; Olszowy *et al.* 1995) and soil quality guidelines (ANZECC and NH&MRC 1992). However, the mean total Cd, Mo, Pb, Sr, Th, U, and Zn concentration plus 1 standard deviation and the median Cd, Mo, Pb, Sr, Th, U, and Zn value of cane soils in the Saltwater Creek catchment exceed those of background soils (Table 2). More importantly, the cane soils have acquired higher Cd/Nb, Mo/Nb, Pb/Nb, Sr/Ti, Th/Nb, U/Nb, U/Ti, and Zn/Ti ratios than the background soils. This implies that the cane soils have obtained their Cd, Mo, Pb, Sr, Th, U, and Zn concentrations from geological bedrock as well as other sources (i.e. atmospheric fall-out of traffic-derived Pb, fertiliser, or mechanised equipment during cultivation and harvesting). In this study, road runoff waters, coal ash, dust from mining and smelting activities, and sewage sludge do not represent possible trace metal sources. Soil samples were collected well away from road structures, there are no coal combustion or mining and smelting activities in the regional area, and sewage sludge is not applied to the agricultural land.

Origin of soil isotope chemistry

The use of Pb isotope data can also resolve ambiguities where natural and anthropogenic sources of Pb cannot be easily distinguished solely on the basis of concentration data. The technique is based on the fact that 3 of the 4 lead isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) are radiogenic and have increased in

abundance with time compared to the non-radiogenic isotope ^{204}Pb . The relative increase for each radiogenic isotope is 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 inputs of Pb (e.g. atmospheric deposition) into the environment, this input commonly causes differences in Pb isotopic ratios in soils, sediments, and waters. Hence, variations in the Pb isotope ratios, such as $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, are commonly used as tracers of environmental contamination processes and as an indicator to differentiate the sources of Pb in environmental samples (Gulson *et al.* 1981, 1994, 1995).

Numerous Pb isotope studies have shown that anthropogenic activities including long- and short-range atmospheric transport and subsequent deposition of anthropogenic aerosols (e.g. from waste incinerators, smelter emissions, and vehicle exhausts) or direct application of waste (e.g. sewage sludge) to agricultural land can lead to Pb contamination of soils (e.g. Hansmann and Köppel 2000; Shotyk *et al.* 2003, 2005; Bacon and Hewitt 2005; Steinnes *et al.* 2005). However, sewage sludges are not applied to the caneland, and possible anthropogenic sources such as smelter stacks, metal refining plants, coal-fired power stations, and waste incinerators are absent in the local and regional area in a ~500 km radius.

Leaded petrol in Australia and road sediments from the Cairns region have distinctly less radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ (~0.93 and 0.916–0.937, respectively) and $^{208}\text{Pb}/^{206}\text{Pb}$ (~2.19 and 2.08–2.11, respectively) ratios than the background forest soils (cf. Gulson *et al.* 1994; Pratt and Lottermoser 2007) (Fig. 5a). The addition of such traffic-derived Pb to cane soils would have resulted in less radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios and a shift in isotope compositions towards leaded petrol (Fig. 5a). By contrast, the results of the soil survey have indicated a shift in the opposite direction towards slightly more radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in cane soils compared with background soils. The cane topsoils exhibit a Pb isotope composition that appears on a mixing line between the isotopically distinct background soils and phosphate fertilisers (Fig. 5a, b). The detected shift in Pb isotope characteristics away from leaded petrol and towards fertiliser compositions can only be accounted for by the addition of fertiliser to cane soils. Yet, the addition of petrol-derived Pb via long- and short-range atmospheric transport and subsequent deposition of aerosols to both cane and forest soils cannot be excluded. Such an input would impact on the isotope composition of both soil types, cane and forest soils, and hence, both soil types may contain petrol-derived Pb.

Mixing calculations of isotope ratios allow the modelling of element sources. Assuming that the applied 1 M HCl extraction releases all soluble Pb and that fertilisers are the sole anthropogenic source of Pb in the cane soils, then the fertilisers provide only ~5% of the total Pb in the cane soils. Such minor addition of Pb is also supported by the fact that the shift in isotope signatures is small (Fig. 2a, b), and that the mean Pb concentration plus 1 standard deviation for forest soils (14.9 ± 5.2 mg/kg) is only slightly different to that of cane soils (25.7 ± 8.7 mg/kg) (Table 2).

Strontium isotopes have largely been used as tracers to establish the sources and fluxes of base cations in soil, water, and plant materials (e.g. Capo *et al.* 1998). By comparison, the use of Sr isotope ratios to track contamination processes on agricultural land has only been pursued to a limited extent (Martin and McCulloch 1999; Hosono *et al.* 2007). These authors measured the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of sediments, soils, and waters from agricultural catchments. The detected Sr isotope changes in samples from cultivated land were interpreted as being due to the application of phosphate fertilisers. Similarly in this study, the limited Sr isotope analyses suggest that the cane soils of the Saltwater Creek catchment possess $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios that are between background soils and phosphate fertilisers (Tables 1, 2). Hence, the observed changes in elemental and isotopic Sr compositions in the investigated cane topsoils are inferred to reflect the addition of fertiliser-derived Sr.

Long-term application of U-bearing fertilisers can elevate the U concentration in fertilised soils (Rothbaum *et al.* 1979; De Kok and Schnug 2008). In this study, the mean U concentration for forest soils (1.83 mg/kg; Table 2) is half than that of cane soils (3.7 mg/kg; Table 2). The data suggest that a significant proportion of the U in the cane soils is fertiliser-derived. Fertiliser-derived U can be recognised using U isotope investigations (Zielinski *et al.* 1997, 2000; Conceição and Bonotto 2003). When rock weathers, ^{234}U is preferentially mobilised to ^{238}U (Ivanovich and Harmon 1992). Consequently, soils that have undergone recent weathering display $^{234}\text{U}/^{238}\text{U}$ activity ratios <1. The mean $^{234}\text{U}/^{238}\text{U}$ ratio of forest soils of the Saltwater Creek catchment corresponded to 0.92, which is a typical value for rocks and soils that have been subjected to recent weathering (Conceição and Bonotto 2003). By contrast, the $^{234}\text{U}/^{238}\text{U}$ activity ratio of cane soils is near unity and identical to that of phosphate fertilisers (Tables 1, 2; Zielinski *et al.* 1997, 2000; Conceição and Bonotto 2003). Therefore, the limited U isotope analyses suggest that there has been fertiliser-derived input of isotopes ^{234}U and ^{238}U to cane soils. Cane soils of the Saltwater Creek catchment have been enriched in fertiliser-derived U.

The investigated forest and cane soils display distinct variations in trace metal contents. These variations cannot be explained by the presence of several different soil types in the catchment. The range of immobile element ratios are restricted in cane and forest soils, demonstrating that both soil sample types derive from the same geological bedrock (i.e. metamorphic rocks). Natural variability in soil chemistry may account for some of the detected elemental variations. However, the Pb, Sr, and U isotopic compositions of soils and fertilisers show that varying proportions of trace metals in cane soils are fertiliser-derived. The Pb isotope data indicate only a minor addition of Pb to agricultural land, whereas the U data imply that much of the U in cane soils is fertiliser-derived. The presence of higher proportions of fertiliser-derived U in cane soils likely reflects the fact that phosphate fertilisers used in north Queensland have much higher U than Pb concentrations (Table 1).

Fate of fertiliser-derived metals

Erosion and leaching of cultivated land potentially led to the transport of fertiliser-derived trace elements into underlying

aquifers or even receiving waterways and the coastal zone, as evidenced for fertiliser-derived Sr and U (cf. Spalding and Sackett 1972; Zielinski *et al.* 1997, 2000; Martin and McCulloch 1999; Conceição and Bonotto 2003; Hosono *et al.* 2007). Thus, agricultural soils and nearby land and water resources are becoming increasingly contaminated by metals due to fertiliser use. Fertiliser-derived trace metals appear to enter terrestrial run-off and they can be tracked using isotope and trace element geochemistry.

This study confirms the presence of fertiliser-derived metals (Cd, Mo, Pb, Sr, Th, U, Zn) within soils of the Saltwater Creek catchment, which feeds into the Great Barrier Reef (GBR) lagoon. Since European settlement, there has been an increase in nutrients and sediments flowing into river catchments and wetland ecosystems that discharge into the GBR lagoon (e.g. Neil *et al.* 2002; McCulloch *et al.* 2003; Devlin and Brodie 2005). The most significant source of diffuse pollution entering the GBR lagoon is overuse/misuse of fertilisers by cropping industries (Reef Water Quality Protection Plan 2003). Further research on the fate and transport of fertiliser-derived metals from topsoils into aquifers, crops, streams, and estuaries of GBR catchments is recommended.

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