Research article

Utilizing Lead Isotope Tracing to Investigate Sustainable Agriculture Practice in the Burdekin Catchment, Australia

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Abstract The Burdekin delta is the largest sugarcane producing region in Australia (85,000 ha) and a major coastal output to the Great Barrier Reef (GBR). Run-off from cultivation areas contain heavy metals from fertilizers, contributing to elevated Cd, Hg, and Pb in waterways. Validating the efficacy of sustainable agriculture practice is necessary to determine if current strategies protect ecosystems and uphold environmental standards. The objective of this study is to utilize Pb isotope tracing ($^{207/206}$Pb and $^{208/206}$Pb) and elevated trace-elements (Cd, Hg, and Pb) as a monitoring tool, to detect residual heavy metals from fertilizers and alternative pollutant sources in the Burdekin catchment. Lead-isotope ratios from dry-season samples of embankment soils/sediment (n=15, 2016, 2019) and water (n=35, 2016-2020), reveals sources of natural forest soils, cane soils (fertilizer enriched), ambient dust, and historic coal fly-ash (Collinsville Power Station). Pb isotope compositions and low levels of heavy metals (soil/sediment: TCd 0.11 mg/kg, THg 0.03 mg/kg and TPb 11.02 mg/kg; estuary: THg 0.011 µg/L and TPb 4.99 µg/L) indicate that fertilizers applied to soils have minimal impact on Burdekin waterways during the dry-season, suggesting effective agricultural practice and sustainable irrigation control.

Keywords agriculture, sustainability, sustainable practice, lead isotope, source-tracing

INTRODUCTION

The GBR is the largest reef ecosystem on the planet (344,400 km^2) and a World Heritage site located off the coast of Queensland (QLD), Australia (Coggan et al., 2021). Land-runoff from coastal catchments can adversely impact the GBR (Lewis et al., 2021). Agricultural mismanagement, (i.e. fertilizer overuse and uncontrolled irrigation run-off) contributes to water quality risk through the accumulation of heavy metals in soil and remobilization to waterways (Table 1; Alengebawy et al., 2021; Coggan et al., 2021). In literature, research has conventionally used elevated heavy metals to establish pollutant presence and Pb-isotopes to trace pollutant source by providing a measure of geologic age (Table 1; Diaz-somoano et al., 2009; Lottermoser, 2009; Alengebawy et al., 2021). Following ~10 years of sugarcane cropping, Rayment (2007) noted Cd and Hg were elevated in QLD cane soils. Davis, et al. (2008) detected sugarcane pesticides in Burdekin waterways. Extended fertilizer use is known to degrade soil fertility and productivity (Ping et al., 2020). Fertilizer overuse burdens the environment, economic and social value of both the GBR and the sugarcane industry (DAE, 2017). Sugarcane production is $1.33 billion AUD (gross); the Burdekin represents 31% or $4.12 million AUD (DAE, 2017). Aboriginal and Torres Strait Islanders have maintained cultural ties to the GBR for ~ 60,000 years. There are over 70 identified clans in the GBR; 16 of which reside in the Burdekin (DAE, 2017). Coastal communities with high fish intake risk methyl-Hg and Cd (neurotoxins) exposure; illustrating community dependence upon ecosystem health (Haswell-Elkins et al., 2006; Russell et al., 2015).

Table 1 Summary of mean cadmium, mercury and lead concentrations (mg/kg) in contaminated soils, fertilizers, sugar cane soil, and sugarcane by-products loading to soil

Description	Cd (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Reference
Fertilizer Derailment				
Contaminated soil (n=7)	4.21	n.a.	53.7	Noller, 2021
Contaminated soil (max)	45	n.a.	790	Noller, 2021
Fertilizer type (N-K-P)				
0-9-0, (n=4)	22	0.5	5.43	Lottermoser, 2009
TSP, 0-21-0	6.67	0.5	6.68	Lottermoser, 2009
DAP, 18-20-0 (n=3)	1.18	0.5	0.33	Lottermoser, 2009
13-14-12 plus	0.85	0.5	132	Lottermoser, 2009
Sugarcane soil (± SD)	0.05	0.069	27	Rayment, 2007; 2011
Sugarcane by-product	Cd (kg/ha)	Hg (kg/ha)	Pb (kg/ha)	
Filter Mud	0.011	n.a.	n.a.	Rayment, 2011
Mill Ash	0.003	n.a.	n.a.	Rayment, 2011
Biosolids	0.11	n.a.	n.a.	Rayment, 2011
Soil loading limits	2	n.a.	260	NWQMS, 2000

Note: N-K-P nitrogen, potassium, and phosphorus; SP, superphosphate; TSP, triple superphosphate; DAP, Di-ammonium phosphate; sugarcane by-products load to soil (0-10 cm depth).

OBJECTIVE

This study investigates utilizing analytical indicators (Pb isotopes: $^{207/206}$Pb and $^{208/206}$Pb and heavy metals: Cd, Pb, and Hg) to monitor sustainable agricultural practice and identify impacts of fertilizer to Burdekin waterways. Alternative pollutant sources are also investigated. In this study, appropriate fertilizer use and irrigation run-off control defines sustainable agricultural practice.

METHODOLOGY

The Burdekin catchment (area ~130,400 km^2) resides in the seasonally dry tropics of NE QLD (Fig. 1). The Upper Burdekin is bordered by coastal ranges (750-1070 m height) < 50 km from the coastline and feeds into the largest dammed catchment in QLD, Lake Dalrymple, impounded by the Burdekin Falls Dam (BFD). In the dry-season, lower catchment flow is driven by allocated releases from the BFD (mean ($\bar{x}$) minimum flow volume ± standard error (±se): 4715 ±406 ML/month) and uncontrolled irrigation run-off (QLD Government, 2017). Approximately 75% of surface water diversion schemes go to irrigation of sugarcane agriculture (Lewis et al., 2021). Monsoonal rains govern flow volumes during the wet season ($\bar{x}$ ±se: 1535476 ML ±255826). Extreme flooding events occur annually, resulting in overspill at BFD, dislodging fertilized material, and dispersing heavy metals to waterways. Monitoring of Burdekin River environment health is carried out during the dry season (May-November $\bar{x}$ ±se:101672 ML ±36104) when vehicle access is possible, and samples are safe to collect. Wet season volumes also cause dilution ($\bar{x}$:15 times, 1986-2021) often resulting in undetectable heavy metal concentrations (WMIP, 2022). As a consequence, heavy metal concentrations from the run-off events are likely to pose greatest environmental risk during the dry-season, when perennial river volumes have returned to "steady-state" flows. Embankment soils/sediments (n=15, 0-100 mm depth, 2016, 2019) and water (n=35, unfiltered, 2016, 2018, 2019 and 2020) were sampled in the Upper and Lower (estuary) sub-catchments of the Burdekin watershed during the dry season. Water and sediment samples in 2016 and 2018 (Fig. 1) were collected in June and July to demonstrate dry-season sources of heavy metals, and input of soil seepage, representing concentrations coinciding with fall of the hydrographic curve. Samples in

2019 and 2020 were collected in late November and early December (increase in hydrographic curve). Thus, sample collections in 2019 and 2020 (Fig. 1) captured first flush and post run-off heavy metal concentrations from the start of the wet-season, including any input from agricultural fertilizers.

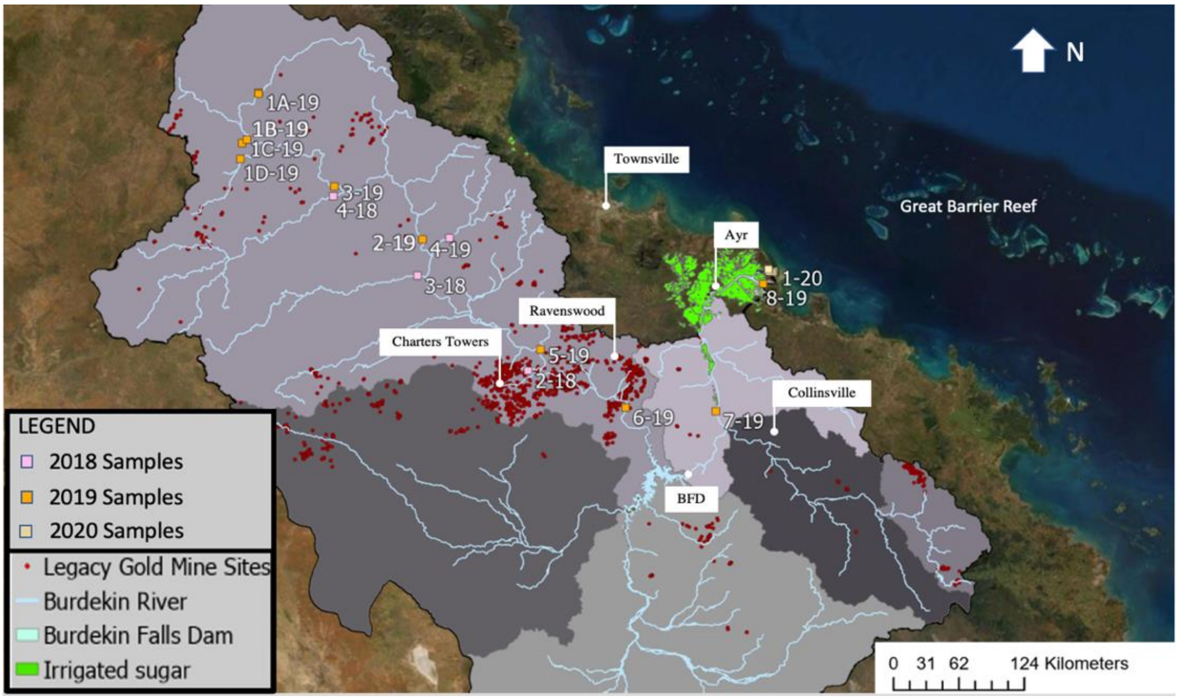

Fig. 1 Study area and sample site location map

Water and soil/sediment were analyzed at the NATA accredited laboratory (ISO/IEC 17025, 2017) Inorganic Chemistry, Queensland Health and Forensic Scientific Services, Coopers Plains, QLD 4108, Australia. Agilent 8800 triple quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ; Agilent Technologies, Santa Clara, CA, USA) measured heavy metal concentrations. Internal standards, spikes and certified reference materials (CRM, TM-28) were used for quality assurance and quality control (QA/QC). QC for Hg analysis used 5% Hg (v/v) HNO_3 solution (SRM ID 3133, SRM Lot # 060204; High Purity Standards, Charleston, SC 29423, USA). Pb isotope ratios ($^{207/206}$Pb and $^{208/206}$Pb) in water, soil and sediment digests were determined by Agilent 8800 ICP-QQQ (CRMs: GXR-1, JG-2, JR-1, JSD-1, JSD-2). Soil/sediment (including CRMs) were prepared following the standard operating procedure (SOP 18191). Water samples were analyzed directly after addition of 0.2 mL High Purity HNO_3 to total 10mL. Pb isotope stock standard solution was used from Choice Analytical and prepared via serial dilution. Ratios were calculated using instrument software. Blank corrections were made with 0.5mL High Purity HNO_3 in 10mL of deionized water. The ICP-QQQ is tuned following manufactures recommendations (Ref 11.3) and QIS: 30638 Operational Guidelines – ICP-MS. Total Hg measurements in soil were analyzed by National Measurement Institute Department of Industry, Innovation and Science, Sydney, Australia.

RESULTS AND DISCUSSION

Mean ±se of total (T) Hg (0.016 ±0.002 μg/L) and TPb (0.15 ±0.02 μg/L) in freshwater remain below ANZG (2018) default guideline values (DGVs) (Table 2). Mercury ($\bar{x}$ ±se: 0.011 ± 0.001) in the estuary are below marine DGVs. In one estuary sample, TPb (4.99 μg/L) is above a marine DGV of 4.4 μg/L (Table 2). At < 2 mm size fraction, embankment soil/sediment samples reflect $\bar{x}$ ±se of TCd (0.11 ±0.10 mg/kg), THg (0.03 ±0.004 mg/kg) and TPb (11.02 ±1.65 mg/kg), all below soil and sediment DGVs throughout the upper and lower catchments (Table 3). The majority of Burdekin soils/sediments (80%) and water (72%) samples, reflect isotopic compositions of cane soil (fertilizer enriched) and natural forest soils (Lottermoser, 2009; Fig. 2A and B). Isotope tracing also suggests TPb Burdekin soils/sediments and waters are reflective of residual coal fly ash and ambient-background dust (Turull et al., 2018). NSW coal fly ash signatures (Fig. 2; Diaz-somoana et al., 2009) identified in Burdekin samples likely reflect historic contributions from a nearby powerplant. A nearby coal-electricity generation station is the Collinsville Power Plant (Fig. 1). Based on current flow statistics, the Burdekin River is highly variable, considerably influencing annual sediment and nutrient loads (Brodie and Bainbridge, 2008). This is apparent in Pb isotope compositions that vary with sample years (Fig. 2B). In 2016, isotope ratios trend toward phosphate-fertilizers and are very similar to ratios found in fertilizer-enriched cultivation areas of the Tully catchment (QLD; Turull et al., 2018). In 2018 and 2019, ratios in fresh and estuarian waters reflect a mixture of sources: NSW coal fly ash, dust, natural forest soils and leaded petrol (1996) (Fig. 2 B).

Table 2 Total Hg and Pb (μg/L) in the Burdekin River from 2016, 2018, 2019, and 2020.

Freshwater	THg (μg/L)	TPb (μg/L)	Saltwater	THg* (μg/L)	TPb (μg/L)
N	24	24	N	11	1
Mean	0.016	0.146	Mean	0.011	4.99
SD	0.01	0.079	SD	0.004	n.a.
SE	0.002	0.018	SEM	0.001	n.a.
Min	0.005	0.053	Min	0.004	n.a.
Median	0.013	0.111	Median	0.011	n.a.
80 percentile	0.022	0.149	80 percentile	0.011	n.a.
95 percentile	0.027	0.204	95 percentile	0.015	n.a.
99 percentile	0.044	0.372	99 percentile	0.018	n.a.
Max	0.048	0.414	Max	0.019	n.a.
Toxicant DGV	0.06[a]	3.4[b]	Toxicant DGV	0.1[a]	4.4[b]

*Note: N, count; SD, standard deviation; SE, standard error, *Collected in 2019 and 2020 n=11,*
[a] 99% level of protection for Hg. [b] 95 % level of protection of species for Pb (ANZG-water, 2018)

Table 3 Total Cd, Hg and Pb (mg/kg), <2mm size fraction soil/sediment from 2016 and 2019

Summary	TCd (mg/kg)	THg (mg/kg)	TPb (mg/kg)
n	14	15	14
No < values	4	9	0
Mean	0.11	0.03	11.02
SD	0.37	0.01	6.16
SE	0.10	0.004	1.65
Min	0.00	0.02	2.40
Median	0.02	0.03	9.13
80 percentile	0.04	0.04	16.00
95 percentile	0.53	0.05	21.10
99 percentile	1.23	0.05	24.22
Max	1.40	0.05	25.00
Toxicant DGV*	1.5	0.15	50

*Note: * No defined level of protection available (ANZG-sediment, 2018)*

BFD stores are replenished during the wet-season from moonsoonal rains (cf. Townsville rainwater $\bar{x}$ ±se: pH 6 ±0.1; Na 1 ± 4 mg/L, Cl 17 ±7 mg/L, from seawater) and released in the dry season for irrigation (Crosbie et al., 2012). Site 7-19 samples, taken below BFD, captures wet-season water stores from dam releases. This is evident in 7-19 water characteristics, where pH and electrical conductivity (EC) are influenced by wet-season rains ($\bar{x}$ ±se pH 7.4 ±0.01, EC: 193 ±1.1 μS/cm). Upstream (dry season) waters ($\bar{x}$ ±se pH 8.5 ±0.02, EC: 558 ±21.1 μS/cm) have higher alkalinity/hardness and EC demonstrating differences between wet/dry waters. In the dry season, heavy metal re-mobilization from sugarcane areas has low environmental, economic and social risk; with one sample, TPb of 4.99 μg/L (2019), above DGVs of 4.4 μg/L (Table 2). Isotope tracing reveals that fertilizer signals remain low throughout the catchment, suggesting sustainble irrigtion practice and run-off control. The impact of fertilizer use in this study is likely minimized due to a delayed start to the wet season in 2019 and 2020 resulting in reduced rainfall run-off events. It is recommended that on-land investigations should be carried out to further inform on fertilizer rates.

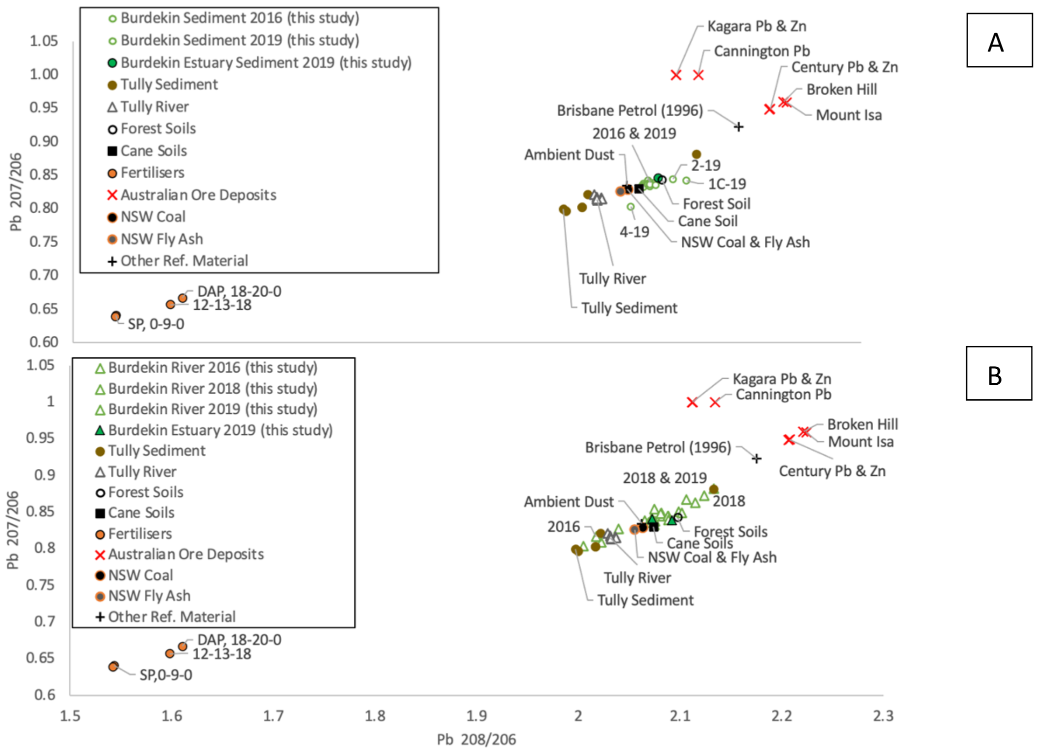

Fig. 2 Pb isotope ratios, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, suggest natural and anthropogenic sources (A) soil/sediment (2016 and 2019) and (B) water (2016, 2018 and 2019)

CONCLUSION

This study informed on baseline heavy metal concentrations and provides new insights of alternative anthropogenic sources impacting Burdekin River water quality (i.e. Collinsville Power Plant). Pb isotope tracing and elevated trace elements is effective at monitoring irrigation control. Fertilizer use has no impact on the Burdekin River in the dry season, suggesting low environmental, economic and social risk. Future land-based investigations could further inform on fertilization rates and impact.

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