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Impact on the environment from steel bridge paint deterioration using lead isotopic tracing, paint compositions and soil deconstruction

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HIGHLIGHTS

- Soil Pb values up to 1200 mg/kg below Pb painted bridge
- Microscopy & SEM characterised up to 6 different paint layers.
- Isotopes identified different sources of Pb including paint and gasoline.
- Multiple methods provide definitive answers.

GRAPHICAL ABSTRACT

Story Bridge Brisbane **TIMS for Pb isotopes** **SEM/EDX**
(By Balhannah http://www.virtualtourist.com/travel)

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ABSTRACT

Deterioration and repair of lead paint on steel structures can result in contamination of the ambient environment but other sources of lead such as from past use of leaded paint and gasoline and industrial activities can also contribute to the contamination. Using a combination of high precision lead isotopic tracing, detailed paint examination, including with scanning electron microscopy, and soil deconstruction we have compared paint on a steel bridge and bulk soil and lead-rich particles separated from soil. The majority of Pb found in the paint derives from Australian sources but some also has a probable US origin. The isotopic data for the bulk soils and selected particles lie on a mixing line with end members the geologically ancient Broken Hill lead and possible European lead which is suggested to be derived from old lead paint and industrial activities. Data for gasoline-derived particulates lie on this array and probably contribute to soil Pb. Although paint from the bridge can be a source of lead in the soils, isotopic tracing, paint morphology and mineralogical identification indicate that other sources, including from paint, gasoline and industrial activities, are contributing factors to the lead burden. Even though physical characteristics and elemental composition are the same in some particles, the isotopic signatures demonstrate that the sources are different. Plots using $^{206}Pb/^{208}Pb$ vs $^{206}Pb/^{207}Pb$ ratios, the common representation these days, do not allow for source discrimination in this investigation.

1. Introduction

Steel bridges and water towers were previously coated with Pb-bearing paints including 'red Pb' (Pb_3O_4). The ambient environment

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around these structures could be contaminated with Pb and other metals from deterioration of the paint over time and as a result of paint removal (Landrigan et al., 1982; Lange, 2002; Lange and Thomulka, 2000; Spee and Zwennis, 1987; Waller et al., 1994). Cases have been described where animals grazing below bridges undergoing repair were Pb poisoned and in some cases animals died. This can also be of concern if there are dwellings in the close proximity of the bridge, including child care centres. In all cases, no attempt was made in historical times to minimise contamination of the surrounding areas.

Previous monitoring of the environment, if undertaken at all, was based on Pb and occasionally other metal concentrations. An alternative approach to monitoring is the use of Pb isotopic tracing. Eckel et al. (2002), Rabinowitz and Hall (2002) and Rabinowitz (2002) employed isotopic tracing to investigate the source Pb in various US paints. We present data from a bridge to investigate the sources of Pb in soil below bridges and demonstrate an approach using Pb isotopic tracing, complemented by optical and scanning electron microscopic examination of soil and particles, to evaluate contamination of the environment around steel bridges containing Pb paint.

2. Materials and methods

We have investigated several bridges and their environment in Australia, including two in Sydney (Sydney Harbour Bridge and Ryde Bridge) and that of the present study in Brisbane (Kangaroo Point under the Story Bridge). Soils collected in 1995 from below the Story Bridge, which was constructed in 1939, were analysed in order to evaluate the source of the elevated Pb levels in the soil. Sample locations are shown in Fig. 1.

The Pb isotopic compositions of paint samples cut using a stainless steel blade from different spans of the bridge (Fig. 1) were compared with randomly collected soil samples usually from the yards of private dwellings. In the case of Kangaroo Point, additional soil samples were collected from a Brisbane City Council borehole programme from either the 0–100 mm or 0–200 mm depths. The site investigation report identified soils containing up to 1200 mg/kg below Story Bridge.

High precision Pb isotopic ratios were measured using thermal ionisation mass spectrometry (TIMS). The methods of analysis have been described in several publications including Gulson et al. (1995). From replicates of the US National Institute of Standards and Technology standard SRM 981 and natural samples, a precision of better than ±0.05% (2σ) for the $^{206}Pb/^{204}Pb$ ratios can be obtained and higher precision can be obtained for the other ratios $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ whose values are closer to 2 and 1 respectively, as against a value of say 16 for the $^{206}Pb/^{204}Pb$ ratios. To enable comparisons of data between laboratories, the isotopic ratios were normalized to the accepted values of the NIST standard SRM 981 (e.g., Todt et al., 1996).

Paint layers were prepared as polished epoxy blocks, examined by reflected light microscopy and scanning electron microscopy (SEM). Lead particulates in the soil were determined with a series of tests and concentration methods which included: sieving at 100 μm with nylon sieves; heavy liquid separation by centrifuging with methylene iodide (SG 3.2); chromatography staining methods to aid Pb particle identification, and microscopic methods which included binocular microscopy for colour, morphology and optical properties and SEM for particle size, morphology and elemental chemical composition. After inspection of the samples by optical microscopy, dominant populations of Pb-bearing particles were handpicked from the soils and prepared for SEM analyses by standard methods. Chemical compositions were measured by EDX with a Cambridge Stereoscan SEM. Some of these particles were also handpicked for Pb isotopic analysis.

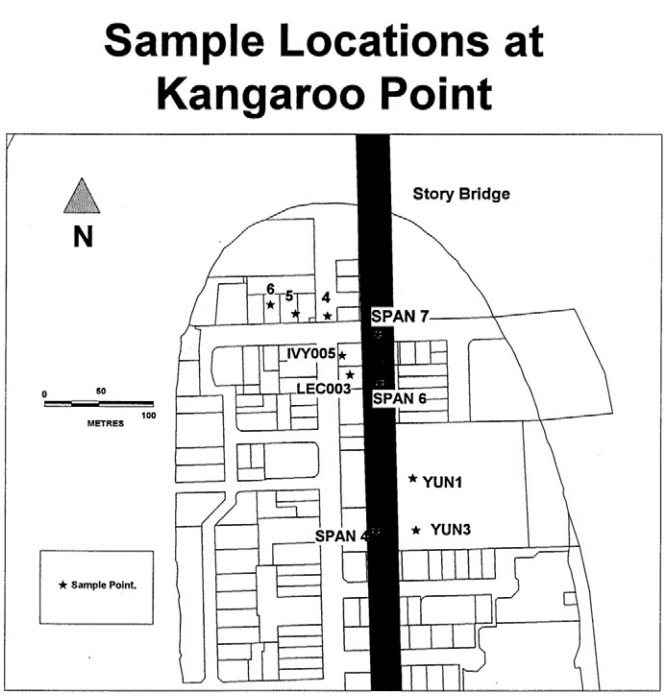

Fig. 1. Location of samples used in this investigation.

3. Results and discussion

The results are listed in Table 1 and Supplementary Tables S2–3 and illustrated in conventional isotopic ratio plots in Fig. 2. Lead concentrations in the analysed soils ranged from 100 to 1200 mg/kg. The isotopic

Table 1
Lead isotopic data for samples from Kangaroo Point, Brisbane.

Sample	208/206	207/206	206/204	Pb (mg/kg)	Colour
Bulk soils					
K. Park #4-1	2.1637	0.9070	17.08	100	
K. Park #4-2a	2.1736	0.9103	17.03		
K. Park #4-2b	2.1731	0.9101	17.01		
K. Park #5-1	2.1267	0.8798	17.69	230	
K. Park #5-2	2.1292	0.8806	17.67		
K. Park #6-1	2.1065	0.8646	18.03	1200	
K. Park #6-2	2.1090	0.8658	18.02		
LEC003 (0–100 mm)	2.1642	0.9116	16.99	>600	
IVY005 (0–100 mm)	2.1591	0.9040	17.18	>600	
YUN 1 (0–200 mm)	2.1862	0.9288	16.65	220	
YUN 3 (0–200 mm)	2.1646	0.9121	16.99	330	
Bulk paint from Story Bridge					
Span 4—lower lateral	2.2092	0.9498	16.23		or
Span 6—lower lateral	2.1613	0.9188	16.84		or
Span 7—sway frame	2.2263	0.9610	16.01		or
Paint layers from Story Bridge					
A (span 4)—layer 5	2.2261	0.9609	15.99	>5%[a]	or
B (span 6)—layer 2	1.9476	0.7837	20.15	<1%[a]	or/red
C (span 6)—layer 6	1.9707	0.7959	19.80	<1%[a]	or
D (span 7)—layer 5	2.2242	0.9605	15.96	>20%[a]	or
Grains handpicked from soils[b]					
E (LEC 003)-a	2.2310	0.9619	16.03	~8%	or
E (LEC 003)-b	2.2313	0.9620	16.04		
F (LEC 003)	2.2250	0.9599	16.01	~20%	or/red
G (IVY 005)	2.0932	0.8509	18.35	~4%	wh/cr
H (#5)	2.0881	0.8499	18.33	~50%	black
J (#5)	2.0896	0.8502	18.34		red
K (#6)	2.1050	0.8620	18.12	~3%	white
L (YUN 1)	2.2273	0.9608	16.01	~50%	wh/cr
M (YUN 3)	2.2271	0.9609	16.02	~6%	wh/cr

-1 and -2, repeat analysis of new sample.
-a and -b, repeat mass spectrometer analysis.
or, orange; wh, white; cr, cream.
[a] Estimations as weights of analysed samples not available.
[b] Lead concentration approximate as weights estimated from size of grains.