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Lead isotope fingerprinting used as a tracer of lead pollution in marine sediments from Botany Bay and Port Hacking estuaries, southern Sydney, Australia

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Anthropogenic lead has been released into environmental ecosystems via human activities; essentially from mining, smelting of lead, leaded gasoline and industrial activities. In order to explore the source apportionment and historic record of lead pollution in the marine sediments, concentration of lead was determined from the Botany Bay and Port Hacking estuaries, south of Sydney, Australia. Areas with the highest concentrations of lead in the sediment samples were analysed by inductively coupled plasma - mass spectrometry (ICP-MS) for lead isotopes to effectively identify the metal contamination source. In addition, other sediment samples were collected from cores at 40cm depth to represent the natural background composition. The study found that the total lead in the tested marine sediments varied from 75.6 mg/kg to 582.2 mg/kg. The $^{206}Pb/^{204}Pb$ showed a decline towards the current surface sediment. Assuming that the natural background source of lead remains the same in terms of both isotopic signature and accumulation rate, the decline in $^{206}Pb/^{204}Pb$ indicated a rise in the contribution of old lead to the sediment, mainly from gasoline fumes (car and boat exhausts) and paint. This is because the samples came from close to water discharge points which have concentrated the catchment lead via stormwater runoff.

Keywords: Marine sediments, lead, Pb isotopes, Enrichment factor, source identification.

1. Introduction

Lead is considered a poisonous metal that is harmful to the human body and can cause serious diseases such central nervous system disorders, kidney brain damage and high blood pressure (Needleman, 2004). Lead pollution above background concentrations in ecosystems is derived from anthropogenic activities such as industry, mining, coal burning, paint and gasoline-fumes. It has increased since the early 1950s from lead-based paints and gasoline-fumes in developed countries, as well as emissions from industrial activities (Needleman, 2004; Gutiérrez-Caminero et al., 2015). It is an important issue in environmental investigation to identify the source of pollution and determine the transport history of

pollutants (Cheng and Hu, 2010). A large number of sources of lead pollution occur in ecosystems, including major contributions from urbanization such as gasoline-air emissions, paints and insecticides, as well as from natural sources such as bedrock (Lu et al., 2011; Zhang et al., 2016). In marine environments, trace metals such as lead can be associated with particulate matter because of their hydrophobic nature and are finally deposited into the underlying sediments (Gerritse et al., 1998). Atmospheric deposition of trace metal pollution is directly documented through several types of environmental ecosystems, such as lake sediments, marine deposits and terrestrial soils (Brännvall et al., 1999; Gobeil et al., 1999; Kelly et al., 2009; Outridge et al., 2011). The distributions of total Pb in sediments can be derived from statistical analysis of a large sample dataset to categorize the source and transport of metal pollution. The chemical composition of trace metals can be an effective method to recognize the source of resources and to compare them by using "fingerprinting" (Qishlaqi and Moore, 2007; Hosono et al., 2016). Several attempts have been made to fingerprint the isotopic composition and ratios of Pb and other metals, which can play an important and powerful tool in tracking sources of pollution (Chiaradia et al., 1997; Franco-Uría et al., 2009; Cheng and Hu, 2010; Popescu et al., 2015; Wen et al., 2015; Hu et al., 2015). Thus, using isotopic ratios of elements is a more sound tracking method than using their concentrations alone to identify sources of contamination (e.g. carbon and chlorine; Sueker, 2001; Philp et al., 2002). In the same way, Pb isotopic composition may be used to trace the source and transport history of Pb (Chiaradia et al., 1997; Cheng and Hu, 2010; Lu et al., 2011; Allan et al., 2015). The main objective of investigating lead isotopes is to support a source apportionment and historic record of lead pollution in the study areas.

2. Methods and Materials

2.1 Study areas

This study covers two coastal areas classified as open estuaries, the Port Hacking and Botany Bay areas in New South Wales, Australia (Fig. 1). The Port Hacking catchment consists of approximately 60% natural bushland with the remainder being urbanised areas. It has a population of approximately 226.220 with a population density of 6 persons per hectare. Contamination is emerging from catchment discharge points as well as recreational activities such as watercraft. Port Hacking contains several bays and some shallow rivers and creeks. Consequently, these deeper bays form sediment traps for fine and very fine particles and detritus that are discharged from the rivers and creeks (Smith et al., 1990). In contrast, the

catchment areas of Botany Bay are urbanised with population estimated at 264.624 and a population density of 28 persons per hectare. The sources of contamination are discharge points, stormwater, farming, fishing, transportation, light industry (including commercial and agricultural), as well as moored watercraft. It is described as a semi-enclosed estuary with a wide coastal embayment that joins with the open sea. The hydrodynamics of Botany Bay have been changed by anthropogenic construction and dredging, which includes the construction of a shipping container port as well as the reclamation effects of Sydney's main airport on the northern side of Botany Bay (Gray et al., 2001; Fraser et al., 2006).
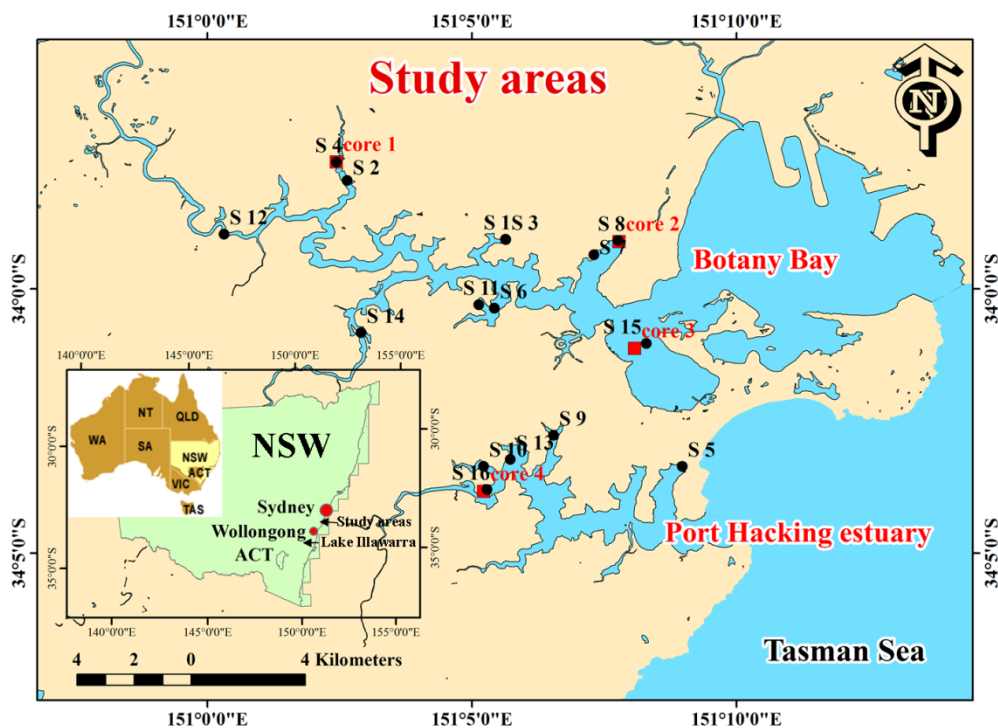

Fig. 1. Surface (dots) and subsurface (red squares) sample locations for lead isotopes in the study areas.

2.2 Sample collection

Surface sediment samples were collected using a grab sampler. The surface 5cm of sediment was reserved for analysis. In addition, subsurface samples were collected using a push core. Fourteen surface sediment samples from the initial 428 samples, which have the highest concentrations of lead, and two samples from a previous study were selected and analysed for lead isotopes. Also, four subsurface sediment samples from different locations were selected to use as background values (Fig. 1 and Table 1). ArcGIS desktop software, version 10.2, was used to create bay boundaries around the collected plot sediment samples of each bay to produce maps for lead, bromine distributions and muddy particles. Spline with Barriers was

chosen as the interpolation method for this part of the analysis due to the ability to input a barrier feature when interpolating a raster surface from points using a minimum curvature spline technique (Lin and Chen, 2004; Lark et al., 2006).

Table 1
Longitude and latitude of sample locations in the study areas.

Sample No.	Longitude	Latitude
S1[a]	323933	6237940
S2	319290	6239903
S3	323946	6237924
S4	318957	6240539
S5	329228	6230085
S6	323656	6235523
S7	326515	6237441
S8	327215	6237954
S9	325459	6231107
S10	323447	6229987
S11	323198	6235637
S12	315737	6237954
S13	324220	6230244
S14	319797	6234596
S15	328102	6234372
S16	323559	6229176
Core 1-40[b]	318957	6240539
Core 2-20	327239	6237907
Core 3-30	327765	6234183
Core 4-40	323462	6229100

[a] Surface sediments and [b] subsurface sediments.

2.2 Analytical methods

Powdered samples were analysed (<4 μm) at the National Measurement Institute (NMI), NSW, Australia. X-ray fluorescence was used to measure concentration of total lead in sediments. Furthermore, approximately 2 gm of each sample was digested in acid (nitric and hydrochloric) then measured for lead using inductively coupled plasma - mass spectrometry (ICP-MS) using a Perkin Elmer Elan DRCll, 1300 W, which has advantages for the analysis of lead isotope ratios in environmental samples (O'Connor and Evans, 2007; Komárek et al., 2008). A summary of the tuning parameters for the ICP-MS equipment, used during measurement of the samples, is presented in Table 2. International reference samples (G-2, BIR-1 and AC-G) were analysed in order to calibrate the precision and accuracy of the analytical procedure. Detection limits for the lead and bromine were 1 mg/kg and 0.5 mg/kg, respectively. Grain size and mud percentages were measured for all sediment samples using a Malvern Mastersizer 2000.

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Table 2
Tuning parameters and implication of the ICP-MS.

Parameters	Typical value/ range He mode
RF Power	1500w
RE matching	1.75 V
Sample depth	8 mm
Torch- H	0.8 mm
Torch- V	0.4 mm
Carrier gas	0.9 l/min
Makeup gas	0.15 l/min
Nebulizer pump	0.1 rps
Extract 1	4 V
Extract 2	-140 V
Omega Bias-ce	-16 V
Omega Lens-ce	1.8 V
Cell Entrance	-24 V
QP focus	-12 V
QP bias	-16V
Cell exit	-30 V

3. Results and Discussion

3.1 Lead concentration in marine sediments

Lead concentrations in surface sediments from the study areas ranged between 75.6 mg/kg and 582.2 mg/kg. The highest concentrations of lead were found in Salt Pan Creek, close to discharge points and around watercraft within the bays, as well as in the inner parts of bays (Fig. 2a). These areas are close to the source of contamination such as stormwater and watercraft, and have high percentages of mud particles and organic matter, indicated by the element bromine (Br) (Fig. 2b and c). In contrast, the lowest concentrations of lead were in the South West Arm and Woronora River that drain natural catchments and are mainly free from residential development. Low concentrations also occur in the mouths, main channel and along the shorelines of the bays (Fig. 2a) because these sites are affected by wave reworking of the sediment that consists predominantly of sand (Fig. 2b). These sites also have low concentrations of Br (Fig. 2c).
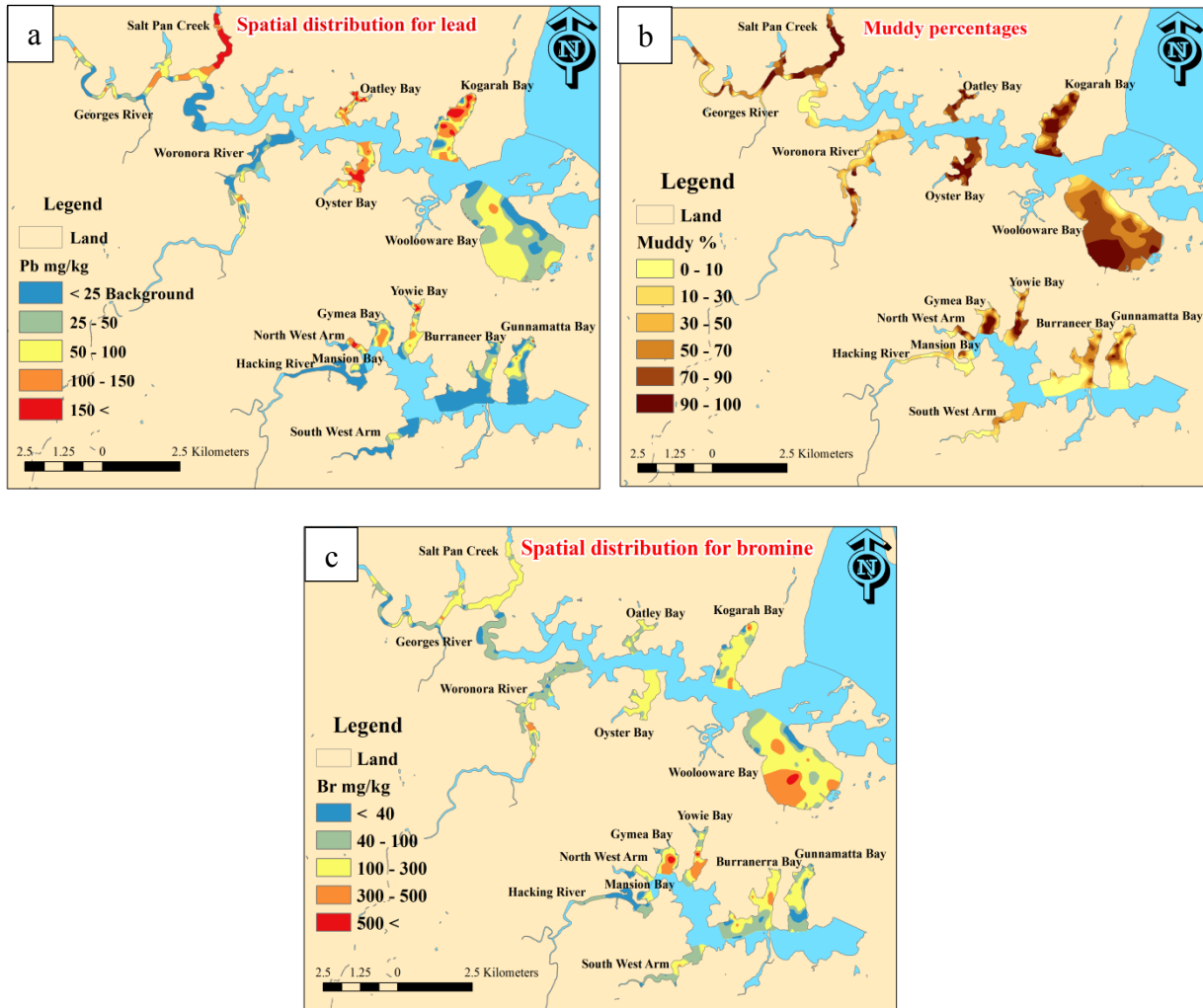
Fig. 2.a- Spatial distribution of lead concentration (mg/kg), **b-**mud percentages and **c-** Br (mg/kg) in the study areas.

Lead concentrations are much lower (4.0 mg/kg to 22.5 mg/kg) within the subsurface sediments. Compared with these background concentrations, the significant increase of lead concentrations in the surface sediments indicates increased contributions of lead from anthropogenic sources. The possibility of sediment and soil pollution is evaluated by the calculation of the trace element enrichment factor (EF), which is commonly used as an indicator for assessing the degree of heavy metal pollution in sediments by normalizing elemental distributions to a reference element. It is a universal formula to distinguish whether the trace element source is anthropogenic or natural Table 3 (Rahman and Ishiga, 2012; Yao et al., 2013; Zhang et al., 2016; Kim et al., 2016). The EFs have been calculated using the following equation:

$$EF = (C_X/C_{Rb})_{sample} / (C_x/C_{Rb})_{background}$$

Where (C_X/C_{Rb}) sample is a ratio of concentration of the element to Rb in the sediment sample; (C_x/C_{Rb}) background is a ratio of the natural background concentrations of the element to Rb. Rubidium (Rb) was used as the trace element of normalization because it is not anthropogenically enriched (Grant and Middleton, 1990). Also, Rb is similar to the value for Ca and higher than the mining interference factor (MIF) for Al and Zr, which are most often used as reference elements (Loska et al., 2004; Mmolawa et al., 2011).

Table 3
Enrichment Factor and its categories.

Enrichment Factor (EF)	Categories
EF < 2	Deficiency to minimal enrichment
2 ≤ EF < 5	Moderate enrichment
5 ≤ EF < 20	Significant enrichment
20 ≤ EF < 40	Very high enrichment
EF ≥ 40	Extremely high enrichment

The enrichment factor for lead in surface sediments is significantly to moderately enriched compared to subsurface sediments (Table 4), which were deficiency to minimal enriched. The EF for Pb varied within bays, with the sources of contamination, such as discharge points for stormwater, as well as the surface sediment sites close to areas that contain boatyards where boats are painted to prevent fouling. There are also large numbers of moored watercraft with potential contaminant spills (Table 4).

3.2 Lead source and apportionment

Although no previous data on lead isotopes had been reported in these study areas, lead isotope signatures have now been determined for the surface and subsurface sediment samples. Pb isotopic compositions can identify the contributions from Pb-containing products such as gasoline-fumes, leaded pesticides and leaded paints (Flament et al., 2002; Vallelonga and Mather, 2003; Cheng and Hu, 2010; Chen et al., 2016). The concentration of lead in the subsurface samples was low at about 15 mg/kg (Alyazichi et al., 2014).

The $^{206}Pb/^{204}Pb$ ratio in these subsurface sediments, below at least 30 cm depth in cores 1 and 3, represents the natural background (pre-European settlement) isotopic signature of about 18.4. This was similar to lead isotope ratios measured in pre-industrial sediment in cores from Lake Illawarra some 80 km south of Sydney (Chenhall et al., 1995; Chiaradia et al., 1997). Between 40 cm and 5 cm, the $^{206}Pb/^{204}Pb$ ratio demonstrated a decline towards the current surface sediment. Assuming that the natural background source of Pb remains the same in

terms of both isotopic signature and accumulation rate of Pb from the source, the decline in $^{206}Pb/^{204}Pb$ suggests a rise in the contribution of old lead to the sediment, mainly from gasoline fumes (car and boat exhausts; Fig. 3a and b).
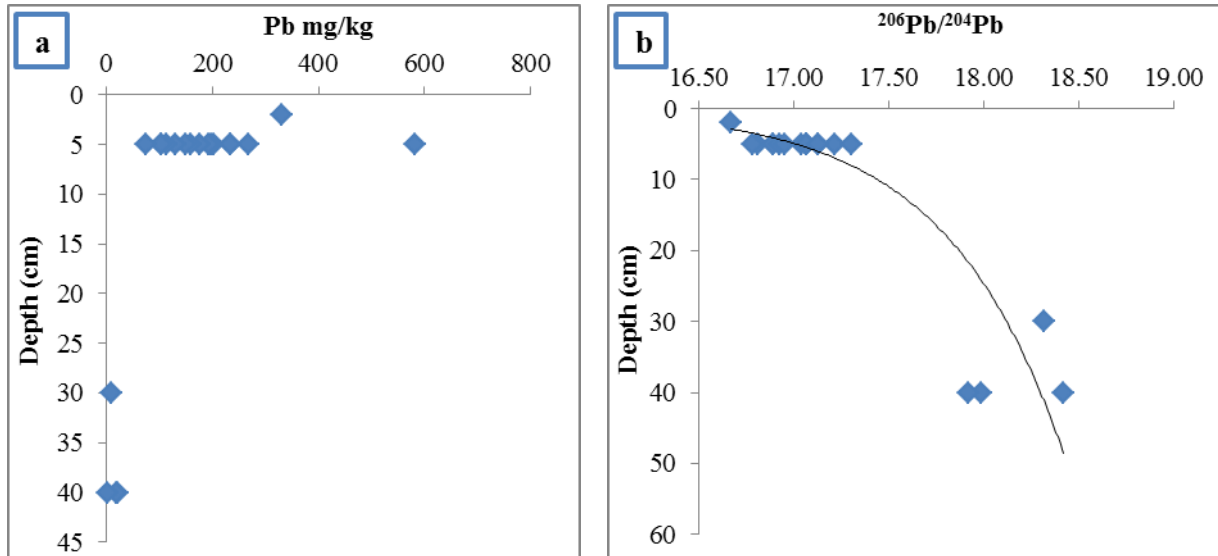

Fig. 3.a-variations of Pb concentrations with sediment depth and **b-** Varitions of $^{206}Pb/^{204}Pb$ ratio with sediments depth in the study areas.

This modification of isotopic composition corresponds to a progressive increase in the concentration of lead from 75.6 mg/kg and 582.2 mg/kg in the upper sedimentary layers (Fig. 3a and b). These changes correspond very well with findings from both roof dust and contaminated sediments from the Lake Illawarra area, where the background $^{206}Pb/^{204}Pb$ Permo-Triassic source similar to the Sydney Basin is about 18.7.

Table 4 represents lead isotopes, lead concentrations in marine sediments, and the calculated contribution of lead from air emissions (i.e. gasoline fumes), which are sourced from vehicles and boats, as well as lead-based paint and industries.

Table 4
Lead isotope data from the study areas and calculated percentage contributions from air-lead (i.e. gasoline fumes).

Sample No.	Depth (cm)	Pb mg/kg	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	Pb air%[d]	EF$_{Pb}$
S 1	5	582.2	0.921	2.173	16.81	82.17	20.7
S 2	5	267.6	0.918	2.174	16.89	78.70	8.4
S 3	5	234.9	0.913	2.168	17.06	71.30	7.8
S 4	5	330.7	0.931	2.188	16.67	88.26	9.4
S 5	5	203	0.925	2.175	16.78	83.48	17.0
S 6	5	198.2	0.909	2.163	17.06	71.30	5.5
S 7	5	235.2	0.912	2.168	17.12	68.70	6.0
S 8	5	193.7	0.916	2.17	16.89	78.70	5.1
S 9	5	176.5	0.914	2.168	16.92	77.39	8.1
S 10	5	158.8	0.914	2.168	16.95	76.09	6.5
S 11	5	149.9	0.91	2.164	17.06	71.30	4.3
S 12	5	131.6	0.906	2.158	17.21	64.78	4.0
S 13	5	113	0.91	2.163	17.30	60.87	4.1
S 14	5	104.9	0.907	2.156	17.04	72.17	2.7
S 15	5	104.1	0.905	2.159	17.06	71.30	3.0
S 16	5	75.6	0.901	2.157	17.12	68.70	3.2
Core 1-40cm	40	22.5	0.866	2.113	17.99	30.87	0.8
Core 2-40cm	40	20	0.848	2.096	18.42	12.17	0.8
Core 3-30cm	30	10.5	0.85	2.102	18.32	16.52	0.7
Core 4-40cm	40	4.0	0.899	2.151	17.92	33.91	2.5
Broken Hill[a]	--	--	0.9617	2.2283	16.003	117.20	--
Mount Isa[b]	--	--	0.9586	2.2224	16.112	112.52	--
Gasoline[c]	--	--	0.9432	2.2015	16.403	99.86	--

[a] (Gulson, 1986)
[b] (Gulson, 1985)
[c] (Gulson et al., 1995).
[d] Pb air % = (18.7$_{Lake\ Illawarra}$ - $^{206}Pb/^{204}Pb_{measured}$) /(18.7 $_{Lake\ Illawarra}$ - 16.4$_{Gasoline}$)*100

Lead isotope ratios in the Botany Bay and Port Hacking sediment samples are represented by $^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$ in (Fig.4; Alyazichi et al., 2014). The surface sample levels lie within and above some samples of roof dust in the Illawarra district (Chiaradia et al., 1997), and below Broken Hill and Mt Isa (old lead deposits in Australia used in the production of leaded petrol), and leaded gasoline fumes (Gulson, 1985, 1986; Gulson et al., 1995). The sub-surface sediment samples (background) from the study areas plot below other samples, except for the samples from Lake Illawarra, with isotope ratios of 2.1 and 0.85 for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, respectively (Fig. 4).

The concentration of Pb in subsurface sediments in the study areas ranged between 4.0 mg/kg and 22.5 mg/kg and the isotopic composition at cores 1 and 3 represent close to natural background sediment from a Palaeozoic source (Chiaradia et al., 1997). Two of the samples from 40 cm show partial contamination by introduced lead probably representing faster

sedimentation rates at cores 1 and 4 or bio-turbation. The lead concentration increased over time towards the surface sediment as a result of anthropogenic contributions. Fig. 4 shows isotope modelling demonstrating that the lead concentrations in surface sediments indicate mixing of natural lead with substantial quantities (60-80%) of gasoline lead (derived from older Broken Hill-Mt Isa lead used in the production of leaded petrol) derived from anthropogenic pollution from both cars and boats.
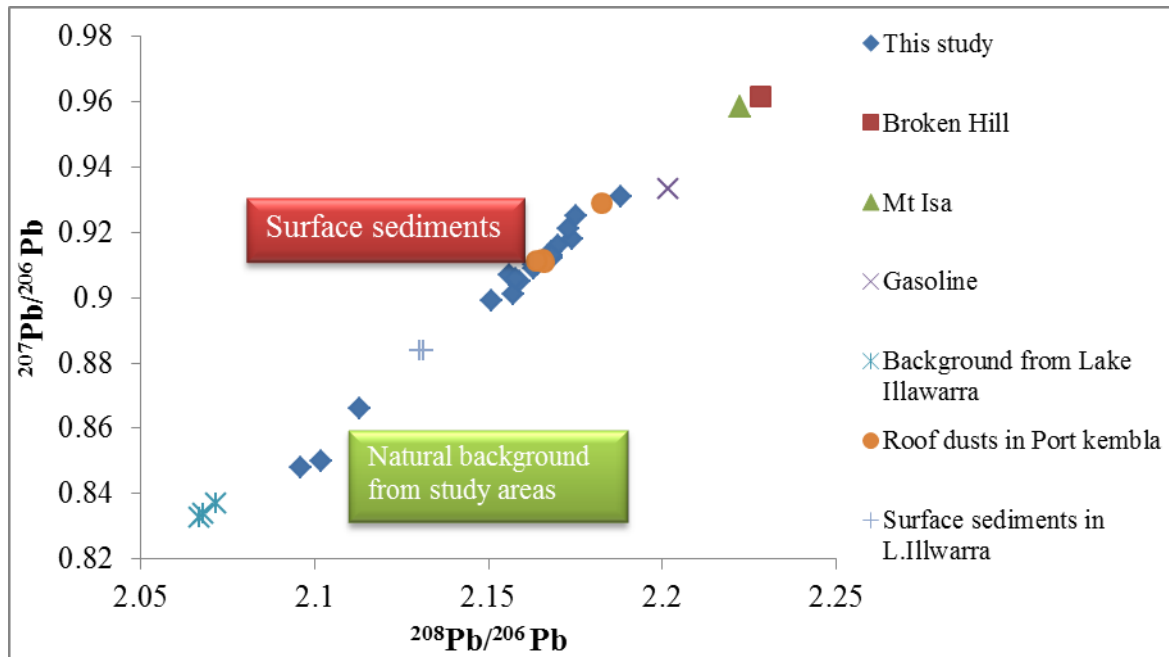

Fig.4. Comparison between ^{207}Pb/^{206}Pb and^{208}Pb/^{206}Pb in different sites.

Conclusions

Our investigation of lead pollution in marine surface sediments from both Botany Bay and Port Hacking estuaries, southern Sydney, indicated a significant increase in surface lead concentrations compared to subsurface sediments. Moreover, the isotopic ratio of ^{206}Pb/^{204}Pb varied from 16.81 at depth 5 cm to 18.42 at a depth of 40 cm. The latter nearly represents natural background isotopic ratios whereas lead isotope modelling demonstrated that the lead concentrations in surface sediments were derived from anthropogenic pollution, especially gasoline fumes from both cars and boats. Between 60-88% of the lead in the surface sediments consists of old Broken Hill or Mt Isa lead derived mainly from leaded paint and gasoline. Continued monitoring of lead concentration in marine sediments and additional sediment samples should be collected for further isotopic study, especially close to discharge points, as well as pleasure boat mooring areas and boatyards. In addition, stormwater outlet remediation devices should be designed with the purpose of decreasing discharges into

estuaries and efficiently removing dissolved toxic elements by using various filters and absorbents.

Acknowledgements

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