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Title: An update of Pb isotope inventory in post leaded-petrol Singapore environments

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ABSTRACT

Pb is a trace metal that tracks anthropogenic pollution in natural environments. Despite recent leaded petrol phase out around Southeast Asia, the region's growth has resulted in continued exposure of Pb from a variety of sources. In this study, sources of Pb into Singapore, a highly urbanised city-state situated in the central axis of Southeast Asia, are investigated using isotopic ratios. We compiled data from our previous analyses of aerosols, incineration fly ash and sediments, with new data from analyses of soil from gas stations, water from runoff and round-island coastal seawater to obtain a spatio-temporal overview of sources of Pb into the Singapore environment. Using $^{206}Pb/^{207}Pb$ ratio, we identified three main Pb source origins: natural Pb (1.215 ± 0.001), historic/remnant leaded petrol (1.123 ± 0.013), and present-day industrial and incinerated waste (1.148 ± 0.005). Deep reservoir sediments bore larger traces of Pb from leaded petrol, but present-day runoff waters and coastal seawater were a mix of both industrial and natural sources. We found temporal variability in Pb isotopic ratio in aerosols indicating alternating transboundary Pb sources to Singapore that correspond to seasonal changes in monsoon winds. By contrast, seasonal monsoon circulation did not significantly influence isotopic ratios of coastal seawater Pb. Instead, seawater Pb was driven more by location differences, suggesting stronger local-scale drivers of Pb such as point sources, water flushing, and isotope exchange. The combination of multiple historic and current sources of Pb shown in this study highlights the need for continued monitoring of Pb in Southeast Asia, especially in light of emerging industries and potential large sources of Pb such as coal combustion.

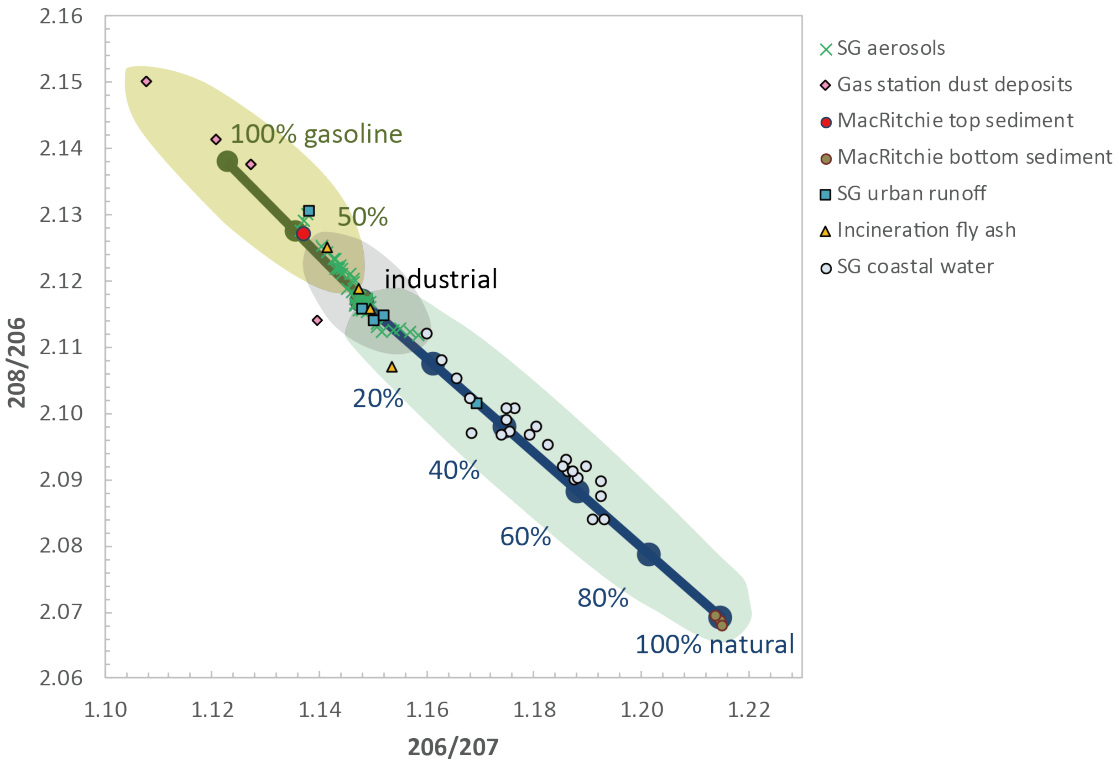
CAPSULE

Pb sources in Singapore are reported as natural, historic leaded petrol and current industrial/incinerator waste based on Pb isotope analyses.

HIGHLIGHTS

- Sources of Pb into Singapore, a highly urbanised city-state situated in the central axis of Southeast Asia, are investigated using isotopic ratios.
- We compile previously reported data (aerosols, incineration fly ash and sediments) with new data (soil from gas stations, water from runoff and round-island coastal seawater) to obtain a spatio-temporal overview of sources of Pb into the Singapore environment.
- Using $^{206}Pb/^{207}Pb$ ratio, we identify three main Pb source origins: natural Pb (1.215 ± 0.001), historic/remnant leaded petrol (1.123 ± 0.013), and present-day industrial and incinerated waste (1.148 ± 0.005).
- Deep reservoir sediments show Pb from leaded petrol, but present-day runoff waters and coastal seawater are a mix of industrial and natural sources.
- Aerosols' temporal variability in Pb isotopic ratios indicates alternating transboundary Pb sources that follow seasonal monsoon changes that contrast with coastal seawater Pb which appears to be driven more by location differences (related to point sources, water flushing, and isotope exchange)

GRAPHICAL ABSTRACT



Triple isotope plot for the Pb in Singapore environments, including aerosols (green crosses), gas station dust deposits (pink diamonds), MacRitchie top and bottom sediments (red and green circles), runoff water (blue squares), incineration fly ash (yellow triangles) and coastal water (open circles). The identified end members are illustrated as gasoline, industrial and natural. The olive-coloured scale bar display the percentage contribution of gasoline if taking the identified 'gasoline' and 'industrial Pb' as end members, the blue-coloured scale bar display the percentage contribution of natural Pb if taking the identified 'natural Pb' and 'industrial Pb' as end members. Shaded areas differentiate the contribution from three identified end members and are for illustration only.

147 INTRODUCTION

148 Anthropogenic lead (Pb) deposited through atmospheric processes has been a
149 major Pb source to various environments (Boutron, 1995; Boyle et al., 2014; Flegal,
150 1986; Komárek et al., 2008). For the past century, the majority of anthropogenic Pb
151 originated from leaded petrol usage and high temperature industrial activities (Nriagu,
152 1989). In more recent years, however, with leaded petrol being globally phased out,
153 along with the increasing industrial activities particularly in developing countries in
154 Asia, there may be great shifts in the relative contributions of Pb sources. This change
155 warrants re-evaluation of regional contributions to the global Pb cycle.

156 Asia has experienced intensive and extensive development in the last two
157 decades. On top of this, the phasing out leaded petrol occurred relatively late in Asian
158 countries (late 1990s to 2000s, UNEP, 2011) – decades after Europe and North
159 America (Kelly et al., 2009). As such, it is important to understand the sources and
160 contribution of Pb in Asian environments to obtain an updated view of global Pb
161 cycle. Numerous studies have attempted to characterize emerging Asian Pb by
162 utilizing Pb isotopes. For example, the Pb isotopes in Asian aerosols before (Bollhöfer
163 and Rosman, 2000) and after (Chen et al., 2005; Duzgoren-Aydin et al., 2004; Lee et
164 al., 2007; Wang et al., 2006; Zhu et al., 2010) the phasing out of leaded petrol have
165 been documented. Asian industrial Pb signatures have also been discovered in North
166 Pacific aerosols and surface waters (Gallon et al., 2011). Temporal variability of
167 Asian Pb has also been shown using numerous sediment cores (Chen et al., 2016a; Li
168 et al., 2012; Liu et al., 2013; Wan et al., 2016; Zhou et al., 2001) and some corals
169 (Chen et al., 2016b; Chen et al., 2015; Inoue et al., 2006; Inoue and Tanimizu, 2008;
170 Lee et al., 2014). Nevertheless, most of these studies have focused on East Asian Pb,
171 while studies from other parts of Asia, particularly Southeast Asia, remain limited,

leaving this as one of the most data-sparse regions in documenting post leaded-petrol Pb sources.

In the current study, we aim to assess the relative contributions of Pb from various sources to a Southeast Asian megacity, Singapore, ~20 years after regional phase out of leaded-petrol. Singapore is highly urbanised and considered one of the most developed city-nations in the region, and home to one of the world's busiest ports (American Association of Port Authorities, 2014). More importantly, Singapore, situated in the central axis of Southeast Asia and flanked by Malaysia and Indonesia – two large and growing sources of Pb to the region (Lee et al. 2014) – is exposed to transboundary Pb sources as monsoonal winds and seawater currents actively ventilate the atmospheric and coastal environments (Figure 1b). Post leaded-petrol isotopic composition of Pb in Singapore's atmospheric, terrestrial, urban, fresh water and marine environments was therefore analysed, i.e. samples from aerosols, surface soils, reservoir sediments, runoff waters and surface seawaters.

MATERIALS AND METHODS

Site information

Singapore is located on the southern tip of the Malay Peninsula, bordered by Malaysia to the north and Indonesia to the south and west (Fig 1). The country is one of the most developed and densely populated cities in the region (Statistics Singapore, 2016) and houses one of the world's busiest ports (American Association of Port Authorities, 2015). Singapore has a monsoonal climate (Singapore National Environmental Agency, 2009): north/northeast wind prevails from December to early March and south/southwest wind prevails from June to September (Meteorological Service Singapore, 2015). Although there are no distinct wet/dry seasons in Singapore, higher

197 rainfall is generally observed during the northeast monsoon period, with peak monthly
198 rainfall (>300mm) in December. Lower rainfall is generally observed from June to
199 September, which coincides with southwest monsoon period (Meteorological Service
200 Singapore, 2015). Due to monsoon-induced currents, the water in the Singapore
201 Straits generally flows westward during northeast monsoon and eastward during
202 southwest monsoon (Pang and Tkalich, 2003; Fig 1b). Singapore phased out leaded
203 petrol in 1997 (Singapore Ministry of Environment, 1987-2000) while neighbouring
204 countries Malaysia and Indonesia phased out leaded petrol in 1998 (Afroz et al., 2003)
205 and 2006 respectively (Chen et al., 2015; Hirota, 2006).
206
207 *Pb sampling*
208 Sampling campaigns for aerosols, incineration ashes, reservoir sediments, urban soils,
209 runoff waters and coastal seawater were carried out between 2010 and 2014 (Table 1,
210 Fig 1). Aerosol samples were collected on a roof of the CREATE building in the
211 National University of Singapore. Aerosols were sampled between 2011 and 2013 by
212 pumping air through a pre-cleaned 0.45μm PTFE filter over at least one week (Chen
213 et al., 2016c). Incineration fly ash samples were collected from Singapore's four
214 incineration plants in December 2010 (Chen et al., 2016b). Among the ash samples,
215 Tuas sample was a mixture of 6-month ash covering June to December 2010; while
216 others were one-day samples. A sediment core was collected in August 2012 from the
217 MacRitchie Reservoir, located in the centre of Singapore, within the central catchment
218 area, using a freeze-corer (Chen et al., 2016a). In order to reconstruct the Pb isotopes
219 in Singapore leaded petrol, soils adjacent to gas stations operational before leaded
220 petrol phase-out date in 1997 were sampled in October of 2014. Soil samples were
221 collected from ~5–10 cm depth to ensure retrieval of material from before the phasing

out of leaded petrol. Four gas stations were sampled, including ESSO and Shell – Singapore's two major petrol suppliers. Runoff water samples were collected in the rainwater drainage channels in November 2014 from various drainage basins in Singapore (Fig 1). The sites are distributed in the north, central, southeast and west of Singapore, covering residential, commercial and industrial areas. During sampling, a trace-metal cleaned bottle was lowered to the water channel using a pole, and water was collected into the pre-cleaned bottle. The water samples were then transported to the lab in a dark cooler and filtered within 24 hours using a trace-metal cleaned 0.4μm Nuclepore polycarbonate filter. The same method was employed for sampling and processing of coastal seawater samples from various sites around Singapore in July and November 2015 that reflect a diversity of natural, industrial and residential sources (Fig 1).

Sample treatment and Pb isotope analysis

All the solid samples (aerosol, ash, sediment, soil) were treated following the method described by Graney et al. (1995). In short, samples were leached by ultrapure 1.75M HNO_3-3M HCl, put in an ultrasonic bath for 60 minutes and then left in room temperature for another 24 hours. The recovery of Pb using this method has been shown to be undistinguishable from concentrated HCl, HNO_3 or Aqua Regia digestions (Graney et al., 1995). The supernatant was extracted; filtered through a 0.4μm membrane; passed through an ion exchange column using Eichrom resin (AG-1X8 chloride form, 200-400 mesh) following the method described in Reuer et al. (2003); and then diluted to an adequate concentration for Pb isotope measurement.

All the water samples were pre-concentrated before analysis. The pre-concentration was done by either evaporation in an acid-cleaned Teflon beaker (for freshwater) or by $Mg(OH)_2$ co-precipitation in a cleaned separation funnel (for seawater). For

247 $Mg(OH)_2$ co-precipitation method, a small volume of isothermally distilled ammonia
248 was added to the sample and the Pb was co-precipitated with $Mg(OH)_2$ (Reuer et al.,
249 2003). The concentrates were re-dissolved in 1.1M HBr and passed through the ion-
250 exchange column as described earlier.
251 After sample pre-treatment, the Pb isotopes in the samples were measured using a
252 multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, G/V
253 Isoprobe) in MIT. Standardizations and corrections of the data were handled as
254 discussed in Boyle et al. (2012). These corrections include: correcting isobaric
255 interferences of ^{204}Hg on ^{204}Pb; correcting procedural and instrumental blanks;
256 correcting instrumental related mass fractionation; correcting dead time of the
257 detector; correcting tailing errors; and normalizing to standard reference materials.
258 Measuring an in-house Pb standard (calibrated with NBS 981 standard reference
259 material) over years gives a relative standard deviation of 160ppm for $^{206}Pb/^{207}Pb$
260 (n=42). Consequently, we report a $^{206}Pb/^{207}Pb$ error of ±0.001 (2 S.E.).
261
262 *Statistical analyses*
263 After testing for normality and homoscedascity in the dataset, a one-way analysis of
264 variance (ANOVA) was used to test for any difference in $^{206}Pb/^{207}Pb$ ratios in aerosol
265 samples taken during the northeast (NE) monsoon (December to March), the
266 southwest (SW) monsoon (June to September) and the inter-monsoon (IM) (April–
267 May and October–November) periods. To test for differences in $^{206}Pb/^{207}Pb$ ratios
268 during the NE vs. SW monsoons in coastal seawater sampled from stations around
269 Singapore, a one-way repeated measures ANOVA was used. All statistical analyses
270 were performed using the statistical program R (version 3.0.3) (R Core Team 2014).

For all data discussed in the manuscript, we are using SE when it refers to errors associated with analytical measurements, and SD when it refers to the standard deviation among averaged samples.

RESULTS

A total of 47 aerosol samples were collected between July 2011 and April 2013 (Fig 3; Table 2). Singapore aerosols $^{206}Pb/^{207}Pb$ ranged between 1.137 and 1.159; while $^{208}Pb/^{206}Pb$ ranged from 2.107 to 2.125. ANOVA of $^{206}Pb/^{207}Pb$ dataset revealed significant differences in Pb ratios between seasons ($F_{2,44}$=9.628, P<0.001): The aerosol $^{206}Pb/^{207}Pb$ during NE monsoon (December to February, 1.150±0.002) was significantly higher than that found during SW monsoon (June to September, 1.145±0.002) and inter-monsoon periods (1.146±0.002) (Fig 3). $^{206}Pb/^{207}Pb$ during the SW and IM periods were not significantly different.

The 40 cm-long sediment core recovered from the MacRitchie Reservoir spanned ~100 years, and showed a decline in $^{206}Pb/^{207}Pb$ from ~1.215 before 1895 to 1.137 in the 1990s (Chen et al., 2016a; Table 1). Concurrently, the $^{208}Pb/^{206}Pb$ increased from ~2.063 before 1895 to 2.122 in the 1990s.

The incineration fly ash samples had $^{206}Pb/^{207}Pb$ of 1.148±0.005 and $^{208}Pb/^{206}Pb$ of 2.111±0.008 (Chen et al., 2015; Table 1).

The $^{206}Pb/^{207}Pb$ in the five runoff samples averaged at 1.152 and fluctuated within 0.011 (Table 1). Among the runoff samples, West Coast Park had the highest $^{206}Pb/^{207}Pb$ (1.169) while Sembawang had the lowest $^{206}Pb/^{207}Pb$ (1.138). The other three sites had similar $^{206}Pb/^{207}Pb$ of ~1.15 (Table 3). The $^{208}Pb/^{206}Pb$ in the runoff samples ranged between 2.096 to 2.126.

295 The Pb ratios for coastal seawater around Singapore averaged ~1.180 for $^{206}Pb/^{207}Pb$,
296 and ~2.091 for $^{208}Pb/^{206}Pb$ (Table 1). The highest $^{206}Pb/^{207}Pb$ was at Changi (1.193),
297 and the lowest at West Coast (1.160) (Table 3). There was no significant difference in
298 the $^{206}Pb/^{207}Pb$ ratios in coastal seawater during the NE vs. SW monsoons ($F_{1,11}$=0.010,
299 P=0.923) –average $^{206}Pb/^{207}Pb$ for both the NE and SW monsoons was 1.180±0.010
300 (Table 3). The $^{208}Pb/^{206}Pb$ was 2.090±0.008 in the NE monsoon season and
301 2.091±0.007 in the SW monsoon (Table 3).
302 The soil samples next to old gas stations had $^{206}Pb/^{207}Pb$ of 1.124±0.013 and
303 $^{208}Pb/^{206}Pb$ of 2.131±0.015 (Table 1; Supplementary Table 1).
304
305 DISCUSSION
306 *Identification of the contributing end-members*
307 The Pb observed in the Singapore environment is likely a combination from several
308 sources, each with possibly a distinct isotopic composition. Identifying the
309 contributing end-members is critical for interpreting Pb isotopes in a suitable
310 framework. The end-members in this context are the ultimate Pb sources that
311 contribute to Singapore environment, which probably includes natural Pb, leaded
312 petrol, industrial sources, and incineration emissions.
313 Natural Pb generated by weathering of the continental crust (Chow and Patterson,
314 1962) could be an important endmember for evaluating the Pb in any environment.
315 The Pb from the bottom 6cm of the MacRitchie sediment core were considered
316 natural because of three reasons: first, the chronology associated with the bottom 6cm
317 of the core implied a period with limited anthropogenic activity. Second, the Pb
318 content in the bottom 6cm of the core was low (1.9 ± 0.6 mg/kg) and the isotopic
319 compositions were unchanging. Third, the Pb isotopes in the bottom 6cm of the core

were consistent with the average continental crust (Chow and Patterson, 1962), the K-feldspars from Asian rivers (Bodet and Schärer, 2001) and the South China Sea abyssal sediments (Zhu et al., 2010). For all the reasons above, the isotopic composition for natural Pb in Singapore was concluded from the bottom 6cm of the MacRitchie sediment core as $^{206}Pb/^{207}Pb$ = 1.215±0.001 and $^{208}Pb/^{206}Pb$ = 2.064±0.001 (Chen et al., 2016a).

Leaded petrol has been phased out around the region (UNEP, 2011) but the historically used petrol could potentially contribute to some environments (i.e. soils, sediments). Because the leaded petrol has been phased out in Singapore for ~10 years (Singapore Ministry of Environment, 1987-2000), measuring the Pb isotopes in Singapore leaded petrol is not possible. Alternatively, the Pb isotopes in Singapore leaded petrol was identified by measuring soils next to old gas stations. The soil samples from Singapore's 4 old gas stations have a generally low $^{206}Pb/^{207}Pb$ (1.124±0.013) (Table 1). The ratio is consistent with the regional aerosols collected when leaded petrol was still in use, including: 1.127±0.001 for Bangkok, 1.131±0.001 for Jakarta, 1.091-1.103 for Bandung, and 1.141±0.001 for Kuala Lumpur (Bollhöfer and Rosman, 2000). Therefore we treat $^{206}Pb/^{207}Pb$=1.124±0.013, $^{208}Pb/^{206}Pb$ = 2.131±0.015 as the isotopic composition in Singapore leaded petrol. However, it should be noted that the actual Pb isotopic composition in Singapore leaded petrol should have slightly lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ to this value as a minor contribution of natural Pb is expected in the collected soil samples.

Industrial sources could be a big contributor to the Pb in Singapore environments, especially after phasing out of leaded petrol. Little is known about the Pb isotopes in Singapore industrial source except incineration. Incinerators in Singapore have been working since 1986 with an increasing capacity in the last decade (Singapore National

Environmental Agency, 2017). Fortunately, the Pb isotopes in the runoff sample from the industrial drainage basin could be an estimate of the industrial sources, with $^{206}Pb/^{207}Pb$=1.152 and $^{208}Pb/^{206}Pb$ = 2.110 (Table 3). The Pb emitted from incineration could be directly represented by fly ash, as $^{206}Pb/^{207}Pb$=1.148±0.005, $^{208}Pb/^{206}Pb$ = 2.112±0.008 (Chen et al., 2015; Table 1). The Pb isotopes in the runoff and the fly ash are almost identical. Consequently, we treat $^{206}Pb/^{207}Pb$=1.148±0.005, $^{208}Pb/^{206}Pb$ = 2.112±0.008 as the isotopic composition from industrial Pb in Singapore.

Sources of Pb in Singapore's atmospheric environment

Singapore aerosol in the 2010s have $^{206}Pb/^{207}Pb$=1.147±0.004, $^{208}Pb/^{206}Pb$ = 2.113±0.004 (Chen et al., 2016a; Table 1). The numbers almost overlap with Singapore industrial Pb and are distinct from leaded petrol in the triple isotope space (Fig 2). Since the isotopic composition of the Singapore aerosols and industrial Pb agree well, we conclude that industrial Pb comprises a major portion of Pb in Singapore aerosols.

The temporal variability of Pb isotopes in aerosols was assessed by the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios. Aerosols collected during the NE monsoon had significantly higher $^{206}Pb/^{207}Pb$ compared to those collected during the SW and inter-monsoon (IM) periods (Fig 3). This seasonal difference implies that in addition to local industrial sources, the atmospheric environment in Singapore is significantly influenced by transboundary Pb sources. During the NE monsoon (December to February), the north-easterly wind brings Pb from the countries to north of Singapore, e.g. China, Vietnam, Cambodia, Thailand and Peninsular Malaysia. The higher $^{206}Pb/^{207}Pb$ found in some recent Chinese aerosols (Chen et al., 2005; Zhu et al., 2010) and a coral off the coast of central Vietnam (Chen et al., 2016b) support such a hypothesis.

Nevertheless, the Pb isotope data from around Asia is still too sparse to pinpoint any particular source. During the southwest monsoon (June to September), the wind potentially brings Pb from the countries to the south, possibly Indonesia. The Pb isotopes in Indonesian aerosols have been reported as 1.091-1.131 for $^{206}Pb/^{207}Pb$ in the 1990s (Bollhöfer and Rosman, 2000), which was slightly lower than the values in Singapore aerosols during the southwest monsoon. However, no value has been reported from Indonesian aerosols after the phasing out of leaded petrol. To conclude from the seasonal variability of Pb isotopes, there are small inter-seasonal differences in Singapore atmospheric sources which could be attributed to transboundary Pb, but the proportion of the contributions is uncertain.

Sources of Pb in Singapore's aquatic environments

In this study, two kinds of water environments were investigated: freshwater environments and coastal environments. For freshwater environments, we sampled a sediment core from the MacRitchie Reservoir and runoff from 5 drainage basins. For coastal environments, we sampled the seawater around Singapore during both monsoon seasons.

Freshwater environment

The surface sediment in the MacRitchie Reservoir (top section of the sediment core) has $^{206}Pb/^{207}Pb$ of 1.137 and $^{208}Pb/^{206}Pb$ of 2.119 (Chen et al., 2016a; Table1). In the triple isotope space, the surface sediment is located in the centre of leaded petrol and industrial sources, which implies that both sources contribute almost equally to the Pb in the MacRitchie top sediment (see scale in Fig 2). It is reasonable to expect some petrol Pb in the sediment as the ^{210}Pb chronology indicates the top part of the sediment

spanning through the 1990s and 2000s (Chen et al., 2016a), which represents an integration of historical freshwater environments in Singapore over the last 20 years.

The Pb isotopes in Singapore runoff show a moderate range, as $^{206}Pb/^{207}Pb$ from 1.138 to 1.169 and $^{208}Pb/^{206}Pb$ from 2.096 to 2.125 (Table 3). The five samples almost form a straight line on the triple isotope space (R^2=0.94, Fig 2). In contrast to the MacRitchie top sediment, most of the runoff sites have Pb isotopes overlapping with recent Singapore aerosols on the triple isotope space (Fig 2). Since industrial Pb is the main source in present day aerosols, the isotopic overlap between Pb in aerosol and runoff water indicates that the Pb in runoff water is also mainly from industrial activities. Comparing the current runoffs with the MacRitchie reservoir surface sediments, a transition of Pb sources from historically used leaded petrol to current industrial sources is observed.

Another feature in the runoff is that except for West Coast Park, the Pb isotope among sites are relatively homogenous, despite strong differences in land use (Table 3). Similar homogeneity was also found in Pb concentration in the road-deposited sediments in Singapore, as the Pb concentration in the sediments from industrial and residential sites were similar (Yuen et al., 2012). The homogeneity implies that the Pb among the sites comes from a similar source, which is likely to be aerosols. To conclude from the homogeneity among sites and the isotopic agreement with aerosols, the Pb in Singapore runoff water is mainly from regional industrial sources through atmospheric deposition.

The water from West Coast Park (WCP) has the highest $^{206}Pb/^{207}Pb$ (1.169) among the runoff sites (Table 3). On the triple isotope space, the WCP water deviates slightly from the aerosols towards natural Pb (Fig 2). The reason for higher $^{206}Pb/^{207}Pb$ was that the sample was taken in an estuary that constantly flushes with seawater. The

seawater in Singapore Straits has systematically higher $^{206}Pb/^{207}Pb$ compared to runoff and will be discussed in the next section.

Marine coastal environment

The seawater around Singapore has $^{206}Pb/^{207}Pb=1.180\pm0.010$ and $^{208}Pb/^{206}Pb=2.091\pm0.007$, and the $^{206}Pb/^{207}Pb$ in seawaters is higher than the runoff (Table 1). On the triple isotope space, seawater falls between industrial Pb and natural Pb (Fig 2), implying both industrial and natural Pb sources contribute to Singapore Straits water. The contribution of natural Pb to Singapore Straits water ranges from ~20% to ~70% (see the scale in Figure 2).

Although we found seasonal differences in $^{206}Pb/^{207}Pb$ for our aerosol samples (Fig 3), no clear trend was found for the coastal seawater samples (Fig 4; Table 3). Over a two-year sampling period (2011-2013) (Table 2; Chen et al., 2016c), the average $^{206}Pb/^{207}Pb$ was almost identical in the NE (1.179±0.011) and the SW (1.180±0.010) monsoons – implying a lack of seasonality in seawater Pb. However, Chen et al. (2016c) have previously proposed an isotope exchange mechanism that could be affecting the results we see here. In brief, crustal particulates with natural Pb isotopic composition are delivered to Singapore waters by rivers in this region, and the Pb on crustal particulates exchanges with the Pb in seawater and alters the seawater Pb isotopes towards natural values. The isotope exchange seems to operate in a much shorter timescale than the residence time of Pb in the Singapore Straits, therefore maintaining the Pb isotope in Singapore Straits' water (Chen et al., 2016c). The proposed isotope exchange mechanism is also supported by the high $^{206}Pb/^{207}Pb$ observed in Johor River mouth (Table 3), which should have the highest concentration of crustal particulates. While we cannot at this point draw any solid conclusions

445 regarding Pb sources Singapore's coastal seawater, our results suggest more local
446 mechanisms driving Pb isotopes in coastal waters – be it through isotope exchange, or
447 the mixing of multiple Pb sources.
448
449 Geographically, stations in the Johor Straits (Kranji, Seletar, Sembawang, Punggol)
450 show slightly lower $^{206}Pb/^{207}Pb$ than those from the Singapore Straits in both seasons
451 (Fig 4; Table 3), indicating more industrial Pb contribution to the northern coastal
452 water. The greater contribution of industrial Pb in the North might not be caused by
453 more industrial activities as the main industrial area in Singapore is located on the
454 southwest side of Singapore near Tuas, which shows $^{206}Pb/^{207}Pb$ towards natural
455 sources (Table 3). Instead, the likely reason for the lower $^{206}Pb/^{207}Pb$ ratios is that less
456 flushing takes place in the North due to the causeway, a dam in the middle of the
457 Johor Straits which interrupts water transport from West to East (see Fig 1). As the
458 water in the North is relatively stagnant, the atmospherically deposited industrial Pb
459 could not be flushed away easily, resulting in a greater contribution of industrial Pb
460 compared to the South. Higher Pb concentration in the surface sediments in the Johor
461 Straits, particularly close to the causeway also supports the idea of limited flushing
462 (Yap et al., 2010).
463
464 CONCLUSION
465 We provide an updated view of sources and variability of Pb in Singapore through
466 exploring the Pb isotopes in various environments, including aerosols, incineration
467 ashes, reservoir sediments, gas station soil deposits, runoff water and coastal seawater.
468 Among these sites, the end members have been identified as leaded petrol, industrial
469 Pb and natural Pb. The three end members contribute in various proportions of Pb in

Singapore's ambient environment. In the atmospheric environment, the Pb in Singapore aerosols is now mainly from regional industrial sources with some transboundary Pb influence indicated by the seasonal variability. In the freshwater environments, we observe a transition of Pb sources from historically leaded petrol in the 1990s to regional industrial sources in the present day. The Pb in Singapore's freshwater environments is likely brought through atmospheric deposition. As such, in a post-leaded petrol Singapore, the concentrations in reservoirs has shown to be below WHO drinking water standard (Chen et al., 2016a). In the coastal environments, we observe significant contributions of Pb from both natural and industrial sources that could be linked to the different water flushing intensity in the Johor and the Singapore Straits.-Natural sources contribute from 20%-70% of Pb in Singapore coastal water. Isotope exchange could potentially be the mechanism for the large contribution of natural Pb to the coastal water.

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Contribution

Gonzalo Carrasco took most of the samples and analysed most of the samples, edited the manuscript.

Mengli Chen took some samples, interpreted the data and wrote the manuscript.

Jani Tanzil took some samples and performed the statistical analyses.

Edward A. Boyle analysed some samples, provided resources and supervision on the project.

Kuanbo Zhou took some samples, edited the manuscript

Nathalie F. Goodkin provided resources and supervision on the seawater sampling cruises.

507 Figures and tables with captions

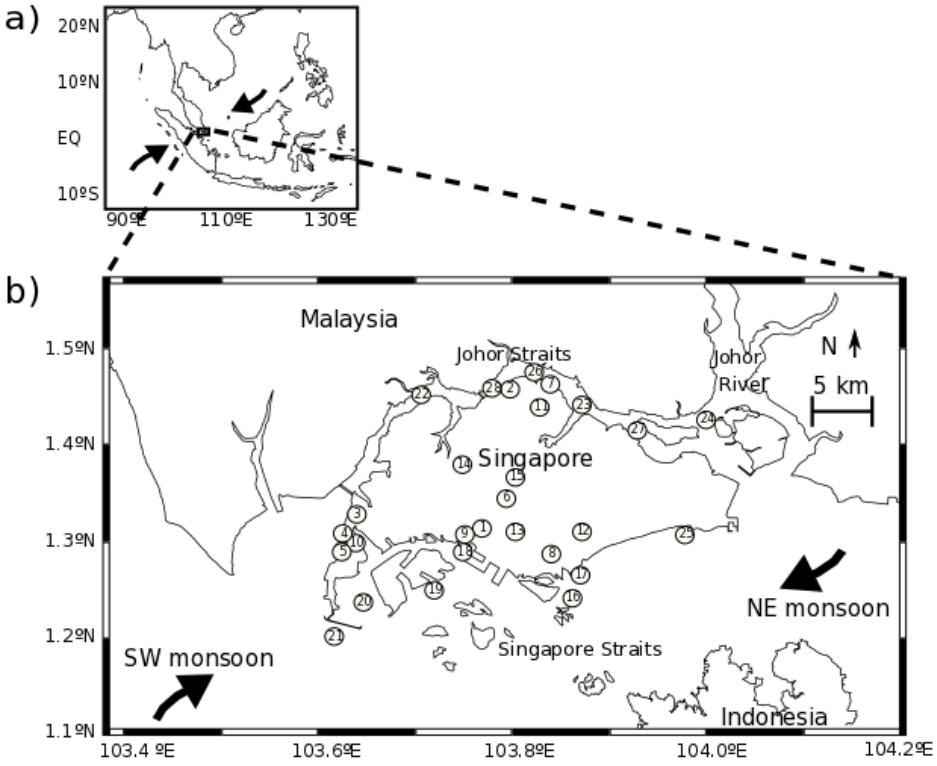

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Figure 1: Map of the sampling sites. (a) Singapore's relative location within Southeast Asia. Arrows denote monsoonal wind directions. (b) Sampling sites within and around Singapore. Aerosols from sampler at NUS (1); ash samples from incinerator plants Senoko (2), Tuas (3), Tuas South (4) and Keppel Seghers Tuas (5); runoff water from Bukit Timah Rd (6), Sembawang Park (7), Raffles place (8), West Coast Park (9) and Tuas industrial park (10); sediments from old gas stations Shell Yishun (11), Shell Geylang (12), ESSO River Valley (13) and ESSO Bukit Panjang (14); sediments from MacRitchie reservoir (15); coastal water from near Kusu island (16), central business district (17), West Coast (18), Jurong island (19), Tuas North (20), Tuas South (21), Kranji (22) , Seletar (23), Johor River mouth (24), Changi (25), Sembawang (26), Punggol (27) and Woodlands (28). Arrows illustrate the direction of monsoonal induced current.

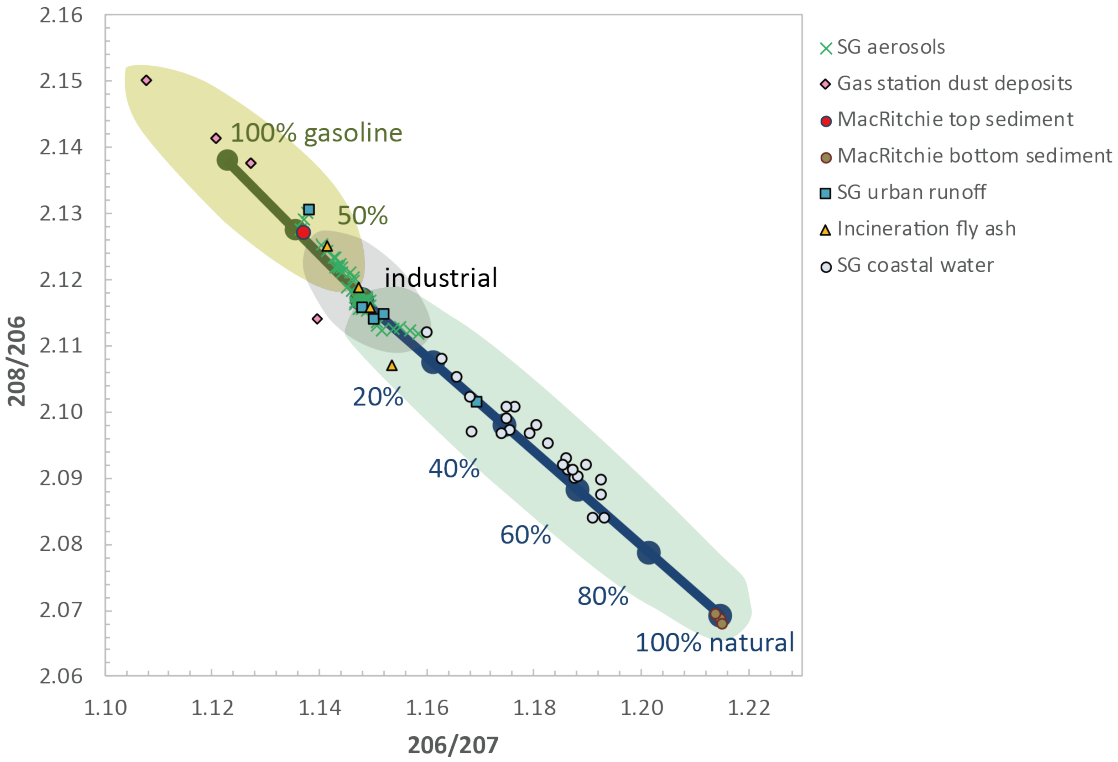

Figure 2: Triple isotope plot for the Pb in Singapore environments, including aerosols (green crosses), gas station dust deposits (pink diamonds), MacRitchie top and bottom sediments (red and green circles), runoff water (blue squares), incineration fly ash (yellow triangles) and coastal water (open circles). The identified end members are illustrated as gasoline, industrial and natural. The olive-coloured scale bar display the percentage contribution of gasoline if taking the identified 'gasoline' and 'industrial Pb' as end members, the blue-coloured scale bar display the percentage contribution of natural Pb if taking the identified 'natural Pb' and 'industrial Pb' as end members. Shaded areas differentiate the contribution from three identified end members and are for illustration only.

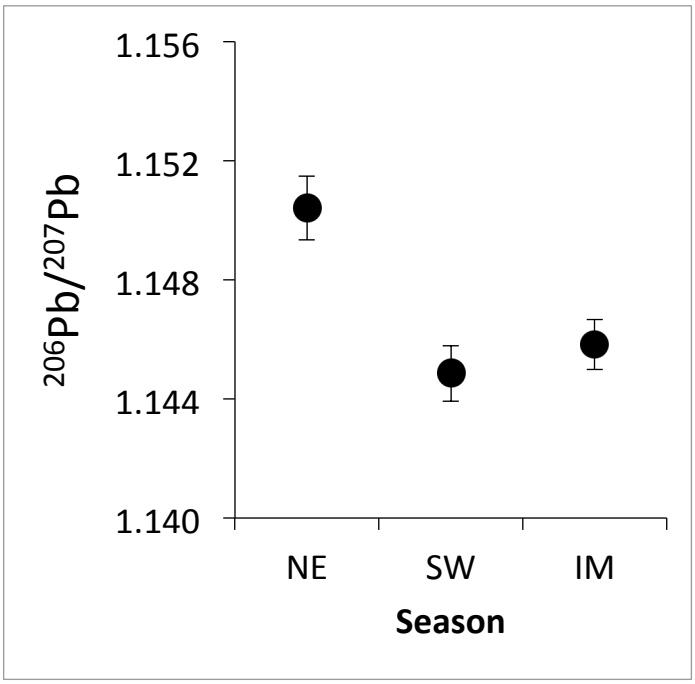

Figure 3: $^{206}Pb/^{207}Pb$ in aerosol samples collected during the northeast monsoon (NE; December–March), southwest monsoon (SW; June–September) and inter-monsoon (IM; April–May and October–November) periods. Error bars denote ± 1SE. ANOVA and Tukey's post-hoc show NE monsoon $^{206}Pb/^{207}Pb$ to be significantly higher than that found for SW monsoon and IM periods.

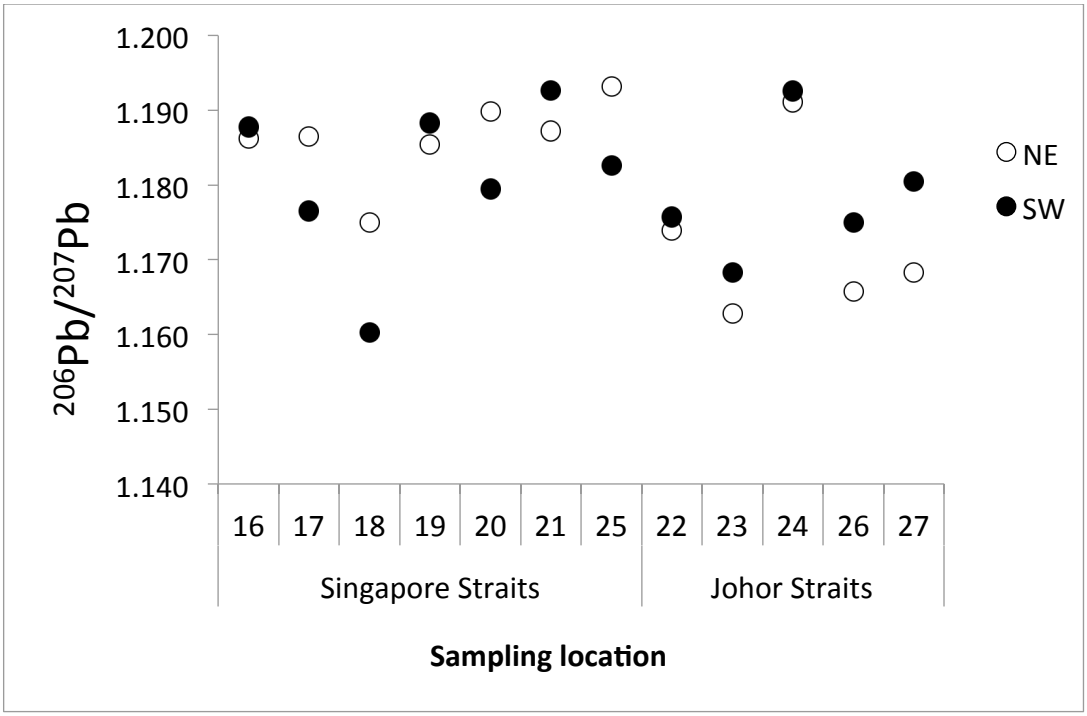

Figure 4: $^{206}Pb/^{207}Pb$ in coastal seawater samples collected during the northeast monsoon (NE; December–March) and southwest monsoon (SW; June–September) from sampling locations around Singapore (along the Johor and Singapore Straits). Kusu island (16), central business district (17), West Coast (18), Jurong island (19), Tuas North (20), Tuas South (21), Kranji (22) , Seletar (23), Johor River mouth (24), Changi (25), Sembawang (26), Punggol (27). See Figure 1 for map of sampling locations.

562 Table 1: An overview $^{206}Pb/^{207}Pb$ ratio among the sampled environments. The end

563 members are identified.

564

Name	*Year samples represent*	*206/207 range*	*206/207 average*	*Representing End Member*	*Source*
Singapore aerosols	2011-2013	1.137-1.159	1.147		Chen et al. (2016)a
Incineration ash	2010	1.141-1.154	1.148	Industrial Pb	Chen et al. (2015)
Runoff water	2014	1.138-1.169	1.152		this study
Gas station soil deposits	1990s	1.107-1.139	1.124	Gasoline Pb	this study
MacRitchie sediment core top	1990s-2012		1.137		Chen et al. (2016)b
MacRitchie sediment core bottom	<1895	1.214-1.215	1.215	Natural Pb	Chen et al. (2016)b
Singapore coastal water	2015	1.160-1.193	1.180		this study

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567 Table 2: Temporal variability of Pb isotope in Singapore aerosols. Data from Chen et

568 al. (2016)a.

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Sampling period	*206/207*	*6/7 2SE*	*208/206*	*8/6 2SE*
July 27-29, 2011	1.1415	0.0001	2.1192	0.0001
August 3-7, 2011	1.1508	0.0000	2.1086	0.0001
August 7-14, 2011	1.1489	0.0001	2.1122	0.0001
August 14-23, 2011	1.1496	0.0001	2.1110	0.0001
August 23-September 16, 2011	1.1488	0.0001	2.1121	0.0001
September 16-October 1, 2011	1.1481	0.0000	2.1117	0.0001
October 1-14, 2011	1.1462	0.0001	2.1133	0.0002
October 14-November 1, 2011	1.1467	0.0000	2.1116	0.0001
November 1-16, 2011	1.1478	0.0001	2.1116	0.0001
November 16-December 16, 2011	1.1467	0.0001	2.1122	0.0001
Dec 16, 2011-Jan 2, 2012	1.1539	0.0003	2.1075	0.0005
January 16-18, 2012	1.1480	0.0003	2.1105	0.0005
February 2-7, 2012	1.1496	0.0001	2.1118	0.0001
February 16-21, 2012	1.1507	0.0001	2.1079	0.0001
March 4-9, 2012	1.1474	0.0001	2.1104	0.0002
March 22-27, 2012	1.1491	0.0000	2.1103	0.0002
April 5-10, 2012	1.1469	0.0001	2.1112	0.0002
April 12-17, 2012	1.1486	0.0001	2.1109	0.0002
April 19- 24, 2012	1.1445	0.0000	2.1160	0.0001

April 26 - May 1, 2012	1.1433	0.0001	2.1169	0.0001
May 3-8, 2012	1.1478	0.0001	2.1115	0.0001
May 10-15, 2012	1.1366	0.0000	2.1225	0.0001
May 17-24, 2012	1.1464	0.0001	2.1152	0.0001
May 24-29, 2012	1.1453	0.0001	2.1139	0.0002
June 1-6, 2012	1.1478	0.0001	2.1125	0.0001
June 11-18, 2012	1.1432	0.0000	2.1182	0.0001
June 18-22, 2012	1.1468	0.0000	2.1123	0.0001
June 28-July 3, 2012	1.1490	0.0003	2.1119	0.0007
July 5-17, 2012	1.1438	0.0000	2.1171	0.0001
July 27-August 1, 2012	1.1477	0.0001	2.1137	0.0001
August 2-7, 2012	1.1464	0.0000	2.1146	0.0001
August 10-15, 2012	1.1372	0.0001	2.1241	0.0001
August 17-23, 2012	1.1377	0.0001	2.1251	0.0002
August 23-29, 2012	1.1437	0.0001	2.1169	0.0001
August 31-September 5, 2012	1.1459	0.0000	2.1160	0.0001
September 6 - 11, 2012	1.1445	0.0000	2.1166	0.0001
September 13-18, 2012	1.1407	0.0000	2.1202	0.0001
September 19-24, 2012	1.1427	0.0000	2.1182	0.0001
November 7-14, 2012	1.1550	0.0000	2.1077	0.0001
November 20-28, 2012	1.1473	0.0000	2.1129	0.0001
November 29-December 4, 2012	1.1518	0.0000	2.1073	0.0001
December 14-19, 2012	1.1432	0.0000	2.1167	0.0001

December 20 - 26, 2012	1.1486	0.0000	2.1109	0.0001
January 3-8, 2013	1.1494	0.0000	2.1095	0.0001
January 16-21, 2013	1.1569	0.0000	2.1072	0.0001
January 24-29, 2013	1.1586	0.0001	2.1068	0.0003
April 12-18, 2013	1.1439	0.0000	2.1172	0.0001

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572 Table 3: Pb isotope in Singapore runoff water and coastal water.

Runoff

Name	*206/207*	*2SE*	*208/207*	*2SE*	*208/206*	*2SE*	*Land use*
Bukit Timah Rd	1.148	0.0002	2.424	0.0003	2.111	0.0002	Residential
Sembawang Park	1.138	0.0008	2.419	0.0011	2.125	0.0010	Shipyard
Raffles place	1.150	0.0001	2.426	0.0002	2.109	0.0002	Commercial
West Coast Park	1.169	0.0001	2.451	0.0003	2.096	0.0002	Residential
Tuas	1.152	0.0004	2.430	0.0007	2.110	0.0006	Industrial

SW monsoon coastal water

Name	*206/207*	*2SE*	*208/207*	*2SE*	*208/206*	*2SE*
Kusu	1.1877	0.0003	2.4763	0.0005	2.0849	0.0004
CBD	1.1765	0.0003	2.4656	0.0007	2.0957	0.0005
West Coast	1.1603	0.0002	2.4446	0.0003	2.1070	0.0003
Jurong island	1.1883	0.0005	2.4778	0.0006	2.0853	0.0006
Tuas North	1.1794	0.0001	2.4669	0.0002	2.0917	0.0002
Tuas South	1.1926	0.0002	2.4863	0.0006	2.0847	0.0004
Kranji	1.1757	0.0004	2.4598	0.0008	2.0923	0.0007
Seletar	1.1684	0.0003	2.4442	0.0006	2.0920	0.0005
Johor River mouth	1.1925	0.0002	2.4834	0.0003	2.0825	0.0003
Changi	1.1827	0.0004	2.4721	0.0007	2.0903	0.0006
Sembawang	1.1750	0.0002	2.4626	0.0004	2.0958	0.0003

Punggol	1.1805	0.0007	2.4708	0.0010	2.0930	0.0009
Mean and SD	1.180	0.010	2.468	0.013	2.091	0.007

NE monsoon coastal water

Name	*206/207*	*2SE*	*208/207*	*2SE*	*208/206*	*2SE*
Kusu	1.1862	0.0004	2.4768	0.0007	2.0880	0.0006
CBD	1.1864	0.0002	2.4752	0.0006	2.0862	0.0004
West Coast	1.1750	0.0003	2.4603	0.0003	2.0939	0.0003
Jurong island	1.1854	0.0003	2.4739	0.0005	2.0869	0.0004
Tuas North	1.1898	0.0002	2.4830	0.0003	2.0869	0.0002
Tuas South	1.1872	0.0003	2.4767	0.0005	2.0861	0.0004
Kranji	1.1739	0.0012	2.4556	0.0018	2.0918	0.0016
Seletar	1.1628	0.0002	2.4453	0.0007	2.1029	0.0005
Johor River mouth	1.1911	0.0003	2.4763	0.0005	2.0789	0.0005
Changi	1.1931	0.0005	2.4806	0.0009	2.0790	0.0007
Sembawang	1.1658	0.0011	2.4483	0.0018	2.1001	0.0015
Punggol	1.1683	0.0002	2.4501	0.0004	2.0972	0.0003
Woodlands	1.1654	0.0002	2.4507	0.0001	2.1028	0.0002
Mean and SD *	1.180	0.011	2.467	0.014	2.090	0.008

573 * excluding Woodlands for the average as it was sampled on one season only

574

575 Supplementary Table 1: Pb isotope in incineration ash from incinerators and gas

576 stations soil deposits around Singapore

Incineration ash

Incinerator	*206/207*	*2SE*	*208/207*	*2SE*	*208/206*	*2SE*
Tuas South	1.1414	0.0011	2.4198	0.0024	2.1200	0.0018
Senoko	1.1496	0.0008	2.4265	0.0006	2.1106	0.0013
Keppel Seglers	1.1535	0.0008	2.4246	0.0011	2.1019	0.0010
Tuas	1.1474	0.0015	2.4253	0.0020	2.1138	0.0019
Mean and SD	1.1480	0.0051	2.4240	0.0030	2.1116	0.0075

Gas station soil deposits

Name	*206/207*	*2SE*	*208/207*	*2SE*	*208/206*	*2SE*
Shell Yishun	1.1077	0.0003	2.3761	0.0003	2.1451	0.0003
Shell Geylang	1.1274	0.0001	2.4042	0.0002	2.1325	0.0002
ESSO CBD	1.1209	0.0001	2.3944	0.0004	2.1362	0.0002
ESSO Bukit Gombak	1.1398	0.0001	2.4037	0.0038	2.1089	0.0024
Mean and SD	1.1240	0.0134	2.3946	0.0131	2.1307	0.0155

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