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

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34 ABSTRACT

35 Pb is a trace metal that tracks anthropogenic pollution in natural environments.  
36 Despite recent leaded petrol phase out around Southeast Asia, the region's growth has  
37 resulted in continued exposure of Pb from a variety of sources. In this study, sources  
38 of Pb into Singapore, a highly urbanised city-state situated in the central axis of  
39 Southeast Asia, are investigated using isotopic ratios and concentrations. We  
40 compiled data from our previous analyses of aerosols, incineration fly ash and  
41 sediments, with new data from analyses of soil from gas stations, water from runoff  
42 and round-island coastal seawater to obtain a spatio-temporal overview of sources of  
43 Pb into the Singapore environment. Using  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, we identified three main  
44 Pb source origins: natural Pb ( $1.215 \pm 0.001$ ), historic/remnant leaded petrol ( $1.123 \pm$   
45  $0.013$ ), and present-day industrial and incinerated waste ( $1.148 \pm 0.005$ ). Deep  
46 reservoir sediments bore larger traces of Pb from leaded petrol, but present-day runoff  
47 waters and coastal seawater were a mix of industrial and natural sources with  
48 somewhat variable concentrations. We found temporal variability in Pb isotopic ratio  
49 in aerosols indicating alternating transboundary Pb sources to Singapore that  
50 correspond to seasonal changes in monsoon winds. By contrast, seasonal monsoon  
51 circulation did not significantly influence isotopic ratios of coastal seawater Pb.  
52 Instead, seawater Pb was driven more by location differences, suggesting stronger  
53 local-scale drivers of Pb such as point sources, water flushing, and isotope exchange.  
54 The combination of multiple historic and current sources of Pb shown in this study  
55 highlights the need for continued monitoring of Pb in Southeast Asia, especially in  
56 light of emerging industries and potential large sources of Pb such as coal combustion.  
57

58 CAPSULE

59 Pb sources in Singapore are reported as natural, historic leaded petrol and current

60 industrial/incinerator waste based on Pb isotope and concentrations analyses.

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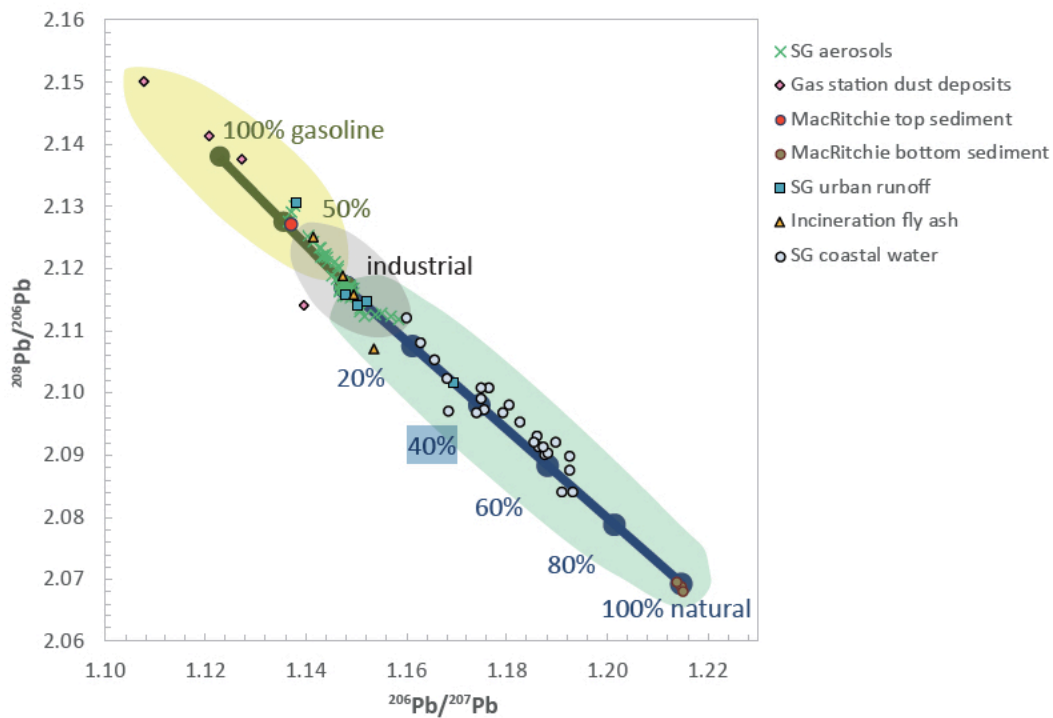
63 HIGHLIGHTS

- 64 • Sources of Pb in Singapore are investigated using isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ )
- 65 • Soils, runoff water, coastal water, aerosols, ashes and sediments studied.
- 66 • 3 sources found: natural, historic leaded petrol and industrial/incinerated waste.
- 67 • Runoff water and coastal seawater are a mix of industrial and natural sources.
- 68 • Processes controlling coastal seawater Pb and aerosol Pb are different.

69

70 GRAPHICAL ABSTRACT

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72

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

83 INTRODUCTION

84 Anthropogenic lead (Pb) deposited through atmospheric processes has been a  
85 major Pb source to various environments (Boutron, 1995; Boyle et al., 2014; Flegal,  
86 1986; Komárek et al., 2008). For the past century, the majority of anthropogenic Pb  
87 originated from leaded petrol usage and high temperature industrial activities (Nriagu,  
88 1989). In more recent years, however, with leaded petrol being globally phased out,  
89 along with the increasing industrial activities particularly in developing countries in  
90 Asia, there may be great shifts in the relative contributions of Pb sources. This change  
91 warrants re-evaluation of regional contributions to the global Pb cycle.

92 Asia has experienced intensive and extensive development in the last two  
93 decades. On top of this, the phasing out of leaded petrol started and was completed  
94 later in Asian countries (late 1990s to 2000s, UNEP, 2011) – decades after Europe  
95 and North America (Kelly et al., 2009), as their respective leaded gasoline Pb  
96 maximum emissions show (Italy in 1971, UK in 1973, France in 1974, Germany in  
97 1970 and the USA in 1972, in contrast to China in 2000, India in 1993, Malaysia in  
98 1982, Indonesia in 1995 and Singapore in 1980, as reported in Kelly et al., 2009, and  
99 Lee et al., 2014). As such, it is important to understand the sources and contribution of  
100 Pb in Asian environments to obtain an updated view of global Pb cycle. Numerous  
101 studies have attempted to characterize emerging Asian Pb by utilizing Pb isotopes.  
102 For example, the Pb isotopes in Asian aerosols before (Bollhöfer and Rosman, 2000)  
103 and after (Chen et al., 2005; Duzgoren-Aydin et al., 2004; Lee et al., 2007; Wang et  
104 al., 2006; Zhu et al., 2010a,b) the phasing out of leaded petrol have been documented.  
105 Asian industrial Pb signatures have also been discovered in North Pacific aerosols and  
106 surface waters (Gallon et al., 2011). Temporal variability of Asian Pb has also been  
107 shown using numerous sediment cores (Chen et al., 2016a; Li et al., 2012; Liu et al.,

108 2013; Wan et al., 2016; Zhou et al., 2001) and some corals (Chen et al., 2016b; Chen  
109 et al., 2015; Inoue et al., 2006; Inoue and Tanimizu, 2008; Lee et al., 2014).  
110 Nevertheless, most of these studies have focused on East Asian Pb, while studies from  
111 other parts of Asia, particularly Southeast Asia, remain limited, leaving this as one of  
112 the most data-sparse regions in documenting post leaded-petrol Pb sources.

113 In the current study, we aim to assess the relative contributions of Pb from  
114 various sources to a Southeast Asian megacity, Singapore, ~20 years after regional  
115 phase out of leaded-petrol. Singapore is highly urbanised, very developed and has  
116 intense port activity. More importantly, Singapore, situated in the central axis of  
117 Southeast Asia and flanked by Malaysia and Indonesia – two large and growing  
118 sources of Pb to the region (Lee et al. 2014) – is exposed to transboundary Pb sources  
119 as monsoonal winds and seawater currents actively ventilate the atmospheric and  
120 coastal environments (Fig 1). Post leaded-petrol isotopic composition and  
121 concentrations of Pb in Singapore’s atmospheric, terrestrial, urban, fresh water and  
122 marine environments were therefore analysed, i.e. samples from aerosols, surface  
123 soils, reservoir sediments, runoff waters and surface seawaters.

124

## 125 MATERIALS AND METHODS

### 126 *Site information*

127 Singapore is located on the southern tip of the Malay Peninsula, bordered by Malaysia  
128 to the north and Indonesia to the south and west (Fig 1a). The country is one of the  
129 most developed and densely populated cities in the region (Statistics Singapore, 2016)  
130 and houses one of the world’s busiest ports (American Association of Port Authorities,  
131 2015). Singapore has a monsoonal climate (Singapore National Environmental  
132 Agency, 2009): north/northeast wind prevails from December to early March and

133 south/southwest wind prevails from June to September (Meteorological Service  
134 Singapore, 2015). Although there are no distinct wet/dry seasons in Singapore, higher  
135 rainfall is generally observed during the northeast monsoon period, with peak monthly  
136 rainfall (>300mm) in December. Lower rainfall is generally observed from June to  
137 September, which coincides with southwest monsoon period (Meteorological Service  
138 Singapore, 2015). Due to monsoon-induced currents, the water in the Singapore  
139 Straits generally flows westward during northeast monsoon and eastward during  
140 southwest monsoon (Pang and Tkalich, 2003; Fig 1b). Singapore phased out leaded  
141 petrol in 1997 (Singapore Ministry of Environment, 1987-2000) while neighbouring  
142 countries Malaysia and Indonesia phased out leaded petrol in 1998 (Afroz et al., 2003)  
143 and 2006 respectively (Chen et al., 2015; Hirota, 2006).

144

#### 145 *Pb sampling*

146 Sampling campaigns for aerosols, incineration ashes, reservoir sediments, urban soils,  
147 runoff waters and coastal seawater were carried out between 2010 and 2014. Aerosol  
148 samples were collected on a roof of the CREATE building in the National University  
149 of Singapore. Aerosols were sampled almost continually between 2011 and 2013 by  
150 pumping air through a pre-cleaned 0.45 $\mu$ m PTFE filter over periods ranging from one  
151 week to one month (Chen et al., 2016c). Incinerator fly ash samples were collected  
152 from Singapore's four incineration plants in December 2010 (Chen et al., 2016b).  
153 Ashes collected were taken from a mixture of levels, and not from the bottom of the  
154 incinerator. Among the ash samples, the Tuas sample was a mixture of 6-month ash  
155 covering June to December 2010; while others were one-day samples. A sediment  
156 core was collected in August 2012 from the MacRitchie Reservoir, located in the  
157 centre of Singapore, within the central catchment area, using a freeze-corer (Chen et

158 al., 2016a). In order to reconstruct the Pb isotopes in Singapore leaded petrol, soils  
159 adjacent to gas stations operational before leaded petrol phase-out date in 1997 were  
160 sampled in October of 2014. Soil samples were collected from ~5–10 cm depth to  
161 ensure retrieval of material from before the phasing out of leaded petrol. Four gas  
162 stations were sampled, including ESSO and Shell – Singapore’s two major petrol  
163 suppliers. No information about the origin of the Pb added to gasoline was obtained,  
164 so different sources could be found. Runoff water samples were collected in the  
165 rainwater drainage channels in November 2014 from various drainage basins in  
166 Singapore (Fig 1). The sites are distributed in the north, central, southeast and west of  
167 Singapore, covering residential, commercial and industrial areas. During sampling, a  
168 trace-metal cleaned bottle was lowered to the water channel using a pole, and water  
169 was collected into the bottle. The water samples were then transported to the lab in a  
170 dark cooler and filtered within 24 hours using a trace-metal cleaned 0.4µm Nuclepore  
171 polycarbonate filter. The same method was employed for sampling and processing of  
172 coastal seawater samples from various sites around Singapore in July and November  
173 2015 that reflect a diversity of natural, industrial and residential sources (Fig 1).

#### 174 *Sample treatment and Pb isotope analysis*

175 All the solid samples (aerosol, ash, sediment, soil) were treated following the method  
176 described by Graney et al. (1995). In short, samples were leached by ultrapure 1.75M  
177 HNO<sub>3</sub>-3M HCl, put in an ultrasonic bath for 60 minutes and then left in room  
178 temperature for another 24 hours. The recovery of Pb using this method has been  
179 shown to be undistinguishable from concentrated HCl, HNO<sub>3</sub> or Aqua Regia  
180 digestions (Graney et al., 1995). The supernatant was extracted; filtered through a  
181 0.4µm membrane; passed through an ion exchange column using Eichrom resin (AG-

182 1X8 chloride form, 200-400 mesh) following the method described in Reuer et al.  
183 (2003); and then diluted to an adequate concentration for Pb isotope measurement.

184 All the water samples were pre-concentrated before analysis. The pre-concentration  
185 was done by either evaporation in an acid-cleaned Teflon beaker (for freshwater) or  
186 by  $\text{Mg}(\text{OH})_2$  co-precipitation in a cleaned separation funnel (for seawater). For  
187  $\text{Mg}(\text{OH})_2$  co-precipitation method, a small volume of isothermally distilled ammonia  
188 was added to the sample and the Pb was co-precipitated with  $\text{Mg}(\text{OH})_2$  (Reuer et al.,  
189 2003). The concentrates were re-dissolved in 1.1M HBr and passed through the ion-  
190 exchange column as described earlier.

191 After sample pre-treatment, the Pb isotopes in the samples were measured using a  
192 multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, G/V  
193 Isoprobe) in MIT. Standardizations and corrections of the data were handled as  
194 discussed in Boyle et al. (2012). These corrections include: correcting isobaric  
195 interferences of  $^{204}\text{Hg}$  on  $^{204}\text{Pb}$ ; correcting procedural and instrumental blanks;  
196 correcting instrumental related mass fractionation; correcting dead time of the  
197 detector; correcting tailing errors; and normalizing to standard reference materials.  
198 Measuring an in-house Pb standard (calibrated with NBS 981 standard reference  
199 material) over years gives a relative standard deviation of 160mg/Kg for  $^{206}\text{Pb}/^{207}\text{Pb}$   
200 ( $n=42$ ). Consequently, we report a  $^{206}\text{Pb}/^{207}\text{Pb}$  error of  $\pm 0.001$  (2 S.E.).

#### 201 *Pb concentration analysis*

202 The concentration of Pb was measured using different methods for each type of  
203 sample. For solid samples (aerosol, ash, sediment, soil), 0.4 $\mu\text{m}$ -filtered Graney  
204 leaches described in the previous section in more detail (Graney et al., 1995) were  
205 diluted and spiked with Indium before being measured in comparison with a multi-  
206 element standard and a Buffalo river sediment standard reference material (NIST) at

207 an 8800 Triple Quadrupole ICPMS (Agilent). For runoff water, as salinity was very  
208 low, samples were spiked with Indium and measured directly at the ICPMS in  
209 comparison with a multi-element standard. For coastal water samples, an isotope  
210 dilution with  $^{204}\text{Pb}$  enriched spike (Oak Ridge National Laboratories) was pre-  
211 concentrated onto nitriloacetate (NTA) resin beads at an ultra-clean ammonium  
212 acetate buffer adjusted pH for 4 days. Resin beads were rinsed of salt 3 times and then  
213 Pb was eluted into high purity 0.1M nitric acid (Fisher Scientific) for 2 days. Finally,  
214 Pb was detected at an 8800 Triple Quadrupole ICPMS (Agilent). These methods are  
215 described in more detail in Lee et al (2014) and Chen et al (2016c).

216

#### 217 *Statistical analyses*

218 After testing for normality and homoscedascity in the dataset, a one-way analysis of  
219 variance (ANOVA) was used to test for any difference in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in aerosol  
220 samples taken during the northeast (NE) monsoon (December to March), the  
221 southwest (SW) monsoon (June to September) and the inter-monsoon (IM) (April–  
222 May and October–November) periods. To test for differences in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios  
223 during the NE vs. SW monsoons in coastal seawater sampled from stations around  
224 Singapore, a one-way repeated measures ANOVA was used. All statistical analyses  
225 were performed using the statistical program R (version 3.0.3) (R Core Team 2014).

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

229 For the estimation of fractions of each end-member (Fig 3), a simple mass balance  
230 equation was used as a mixing model, whereby 2 end-members were taken at a time

231 and using iterative percentages of each component's abundance, points in triple  
232 isotope space were defined along the mixing line.

233

## 234 RESULTS

235 A total of 47 aerosol samples were collected between July 2011 and April 2013  
236 (Supplementary Table 1). Singapore aerosols  $^{206}\text{Pb}/^{207}\text{Pb}$  ranged between 1.137 and  
237 1.159; while  $^{208}\text{Pb}/^{206}\text{Pb}$  ranged from 2.107 to 2.125 (Table 1). ANOVA of  $^{206}\text{Pb}/^{207}\text{Pb}$   
238 dataset revealed significant differences in Pb ratios between seasons ( $F_{2,44}=9.628$ ,  
239  $P<0.001$ ): The aerosol  $^{206}\text{Pb}/^{207}\text{Pb}$  during NE monsoon (December to February,  
240  $1.150\pm 0.002$ ) was significantly higher than that found during SW monsoon (June to  
241 September,  $1.145\pm 0.002$ ) and inter-monsoon periods ( $1.146\pm 0.002$ ) (Fig 2).  
242  $^{206}\text{Pb}/^{207}\text{Pb}$  during the SW and IM periods were not significantly different.

243 The 40 cm-long sediment core recovered from the MacRitchie Reservoir spanned  
244 ~100 years (as dated by the  $^{210}\text{Pb}$  decay gamma radiation counting method), and  
245 showed a decline in  $^{206}\text{Pb}/^{207}\text{Pb}$  from ~1.215 before 1895 to 1.137 in the 1990s (Chen  
246 et al., 2016a; Table 1). Concurrently, the  $^{208}\text{Pb}/^{206}\text{Pb}$  increased from ~2.063 before  
247 1895 to 2.122 in the 1990s.

248 The incineration fly ash samples had  $^{206}\text{Pb}/^{207}\text{Pb}$  of  $1.148\pm 0.005$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  of  
249  $2.111\pm 0.008$  (Chen et al., 2015; Table 1; Supplementary Table 2).

250 The  $^{206}\text{Pb}/^{207}\text{Pb}$  in the five runoff samples averaged at 1.152 and fluctuated within  
251 0.011 (Table 1). Among the runoff samples, West Coast Park had the highest  
252  $^{206}\text{Pb}/^{207}\text{Pb}$  (1.169) while Sembawang had the lowest  $^{206}\text{Pb}/^{207}\text{Pb}$  (1.138). The other  
253 three sites had similar  $^{206}\text{Pb}/^{207}\text{Pb}$  of ~1.15 (Table 2). The  $^{208}\text{Pb}/^{206}\text{Pb}$  in the runoff  
254 samples ranged between 2.096 to 2.126.

255 The Pb ratios for coastal seawater around Singapore averaged  $\sim 1.180$  for  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  
256 and  $\sim 2.091$  for  $^{208}\text{Pb}/^{206}\text{Pb}$  (Table 1). The highest  $^{206}\text{Pb}/^{207}\text{Pb}$  was at Changi (1.193),  
257 and the lowest at West Coast (1.160). There was no significant difference in the  
258  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in coastal seawater during the NE vs. SW monsoons ( $F_{1,11}=0.010$ ,  
259  $P=0.923$ ) – average  $^{206}\text{Pb}/^{207}\text{Pb}$  for both the NE and SW monsoons was  $1.180\pm 0.010$ .  
260 The  $^{208}\text{Pb}/^{206}\text{Pb}$  was  $2.090\pm 0.008$  in the NE monsoon season and  $2.091\pm 0.007$  in the  
261 SW monsoon (Supplementary Table 3).

262 The soil samples next to old gas stations had  $^{206}\text{Pb}/^{207}\text{Pb}$  of  $1.124\pm 0.013$  and  
263  $^{208}\text{Pb}/^{206}\text{Pb}$  of  $2.131\pm 0.015$  (Table 1; Supplementary Table 2).

264 The main focus of this manuscript is to discern the end-members of Pb as determined  
265 by Pb isotope ratios. The concentration values from different media are shown here  
266 for reference and to support the end-members defined using the isotope ratios.  
267 Another manuscript is being prepared focusing on concentrations of Pb and other  
268 trace metals in coastal waters of Singapore. Table 3 presents the Pb concentrations of  
269 gas station soils, runoff and coastal waters.

270 The gas station soils range between 10 and 95mg/Kg, averaging 41mg/Kg, higher  
271 than the bottom of MacRitchie natural values (2mg/Kg as in Chen et al, 2016a) or  
272 Marina Bay Sands 8mg/Kg (not shown).

273 The runoff waters have a large range of concentrations between 20 and 1047pmol/kg  
274 averaging 311pmol/kg as they have represent different types of urban use (residential,  
275 industrial, shipyard). These values are higher and more variable than those determined  
276 for coastal waters in both sampling times. SW monsoon coastal waters are between 45  
277 and 291pmol/kg averaging 141pmol/kg, and NE monsoon waters are between 44 and  
278 181pmol/kg averaging 106pmol/kg.

279

280 DISCUSSION

281 *Identification of the contributing end-members*

282 The Pb observed in the Singapore environment is likely a combination from several  
283 sources, each with possibly a distinct isotopic composition. Identifying the  
284 contributing end-members is critical for interpreting Pb isotopes in a suitable  
285 framework. The end-members in this context are the ultimate Pb sources that  
286 contribute to Singapore environment, which probably includes natural Pb, leaded  
287 petrol, industrial sources, and incineration emissions.

288 Natural Pb generated by weathering of continental crust (Chow and Patterson, 1962)  
289 could be an important end-member for evaluating the Pb in any environment. The Pb  
290 from the bottom 6cm of the MacRitchie sediment core was considered natural because  
291 of three reasons: first, the chronology associated with the bottom 6cm of the core  
292 implied a period with limited anthropogenic activity. Second, the Pb content in the  
293 bottom 6cm of the core was low ( $1.9 \pm 0.6$  mg/kg) and the isotopic compositions were  
294 unchanging (Chen et al., 2016a). Third, the Pb isotopes in the bottom 6cm of the core  
295 were consistent with the average continental crust (Chow and Patterson, 1962), the K-  
296 feldspars from Asian rivers (Bodet and Schärer, 2001) and the South China Sea  
297 abyssal sediments (Zhu et al., 2010a). For all the reasons above, the isotopic  
298 composition for natural Pb in Singapore was resolved from the bottom 6cm of the  
299 MacRitchie sediment core as  $^{206}\text{Pb}/^{207}\text{Pb}=1.215 \pm 0.001$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.064 \pm 0.001$   
300 (Chen et al., 2016a).

301 Leaded petrol has been phased out around the region (UNEP, 2011) but the  
302 historically used leaded petrol could potentially contribute to some environments (i.e.  
303 soils, sediments). Because the leaded petrol has been phased out in Singapore for ~10  
304 years (Singapore Ministry of Environment, 1987-2000), measuring the Pb isotopes in

305 Singapore leaded petrol is not possible currently. Alternatively, the Pb isotope  
306 signature in Singapore leaded petrol was identified by measuring soils next to gas  
307 stations that used to sell leaded gasoline. The soil samples from Singapore's 4 old gas  
308 stations have a generally low  $^{206}\text{Pb}/^{207}\text{Pb}$  ( $1.124\pm 0.013$ ) (Table 1). The ratio is  
309 consistent with the regional aerosols collected when leaded petrol was still in use,  
310 including:  $1.127\pm 0.001$  for Bangkok,  $1.131\pm 0.001$  for Jakarta, 1.091-1.103 for  
311 Bandung, and  $1.141\pm 0.001$  for Kuala Lumpur (Bollhöfer and Rosman, 2000).  
312 Therefore we treat  $^{206}\text{Pb}/^{207}\text{Pb}=1.124\pm 0.013$ ,  $^{208}\text{Pb}/^{206}\text{Pb}=2.131\pm 0.015$  as the isotopic  
313 composition in Singapore leaded petrol. However, it should be noted that the actual  
314 Pb isotopic composition in Singapore leaded petrol should have slightly lower  
315  $^{206}\text{Pb}/^{207}\text{Pb}$  and higher  $^{208}\text{Pb}/^{206}\text{Pb}$  to this value as a minor contribution of natural Pb is  
316 expected in the collected soil samples. The correlation between high Pb concentration  
317 (Table 3) and low  $^{206}\text{Pb}/^{207}\text{Pb}$  and high  $^{208}\text{Pb}/^{206}\text{Pb}$  (Supplementary Table 2) in these  
318 soils provides support for this hypothesis.

319 Industrial sources could be a big contributor to the Pb in Singapore environments,  
320 especially after phasing out of leaded petrol. Little is known about the Pb isotopes in  
321 Singapore industrial source except about incineration. Incinerators in Singapore have  
322 been working since 1986 with an increasing capacity in the last decade (Singapore  
323 National Environmental Agency, 2017). Fortunately, the Pb isotopes in the runoff  
324 sample from the industrial drainage basin could be an estimate of the industrial  
325 sources, with  $^{206}\text{Pb}/^{207}\text{Pb}=1.152$  and  $^{208}\text{Pb}/^{206}\text{Pb}=2.110$  (Table 2). The Pb emitted from  
326 incineration could be directly represented by fly ash, as  $^{206}\text{Pb}/^{207}\text{Pb}=1.148\pm 0.005$ ,  
327  $^{208}\text{Pb}/^{206}\text{Pb}=2.112\pm 0.008$  (Chen et al., 2015; Table 1). The Pb isotopes in the runoff  
328 and the fly ash are almost identical. Consequently, we treat  $^{206}\text{Pb}/^{207}\text{Pb}=1.148\pm 0.005$ ,  
329  $^{208}\text{Pb}/^{206}\text{Pb}=2.112\pm 0.008$  as the isotopic composition from industrial Pb in Singapore.

330

331 *Sources of Pb in Singapore's atmospheric environment*

332 Singapore aerosols in the 2010s have lead isotopes defined as  
333  $^{206}\text{Pb}/^{207}\text{Pb}=1.147\pm 0.004$ ,  $^{208}\text{Pb}/^{206}\text{Pb}=2.113\pm 0.004$  (Chen et al., 2016a; Table 1). The  
334 numbers almost overlap with Singapore industrial Pb and are distinct from leaded  
335 petrol in the triple isotope space (Fig 3). Since the isotopic composition of the  
336 Singapore aerosols and industrial Pb agree well, we conclude that industrial Pb  
337 comprises a major portion of Pb in Singapore aerosols.

338 The temporal variability of Pb isotopes in aerosols was assessed by the  $^{206}\text{Pb}/^{207}\text{Pb}$   
339 and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios. Aerosols collected during the NE monsoon had significantly  
340 higher  $^{206}\text{Pb}/^{207}\text{Pb}$  compared to those collected during the SW and inter-monsoon (IM)  
341 periods (Fig 2). This seasonal difference implies that in addition to local industrial  
342 sources, the atmospheric environment in Singapore is significantly influenced by  
343 transboundary Pb sources. During the NE monsoon (December to February), the  
344 north-easterly wind brings Pb from the countries to north of Singapore, e.g. China,  
345 Vietnam, Cambodia, Thailand and Peninsular Malaysia. The higher  $^{206}\text{Pb}/^{207}\text{Pb}$  found  
346 in some recent Chinese aerosols (Chen et al., 2005; Zhu et al., 2010b) and a coral off  
347 the coast of central Vietnam (Chen et al., 2016b) support such a hypothesis.  
348 Nevertheless, the Pb isotope data from around Asia is still too sparse to pinpoint any  
349 particular source. During the southwest monsoon (June to September), the wind  
350 potentially brings Pb from the countries to the south, possibly Indonesia. The Pb  
351 isotopes in Indonesian aerosols have been reported as 1.091-1.131 for  $^{206}\text{Pb}/^{207}\text{Pb}$  in  
352 the 1990s (Bollhöfer and Rosman, 2000), which was slightly lower than the values in  
353 Singapore aerosols during the southwest monsoon. However, no value has been  
354 reported from Indonesian aerosols after the phasing out of leaded petrol. To conclude

355 from the seasonal variability of Pb isotopes, there are small inter-seasonal differences  
356 in Singapore atmospheric sources which could be attributed to transboundary Pb, but  
357 the proportion of the contributions is uncertain.

358

#### 359 *Sources of Pb in Singapore's aquatic environments*

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

364

#### 365 Freshwater environment

366 The surface sediment in the MacRitchie reservoir (top section of the sediment core)  
367 has  $^{206}\text{Pb}/^{207}\text{Pb}$  of 1.137 and  $^{208}\text{Pb}/^{206}\text{Pb}$  of 2.119 (Chen et al., 2016a; Table1). In  
368 triple isotope space, the surface sediment is located in the centre of leaded petrol and  
369 industrial source end-members, which implies that both sources contribute almost  
370 equally to the Pb in the MacRitchie top sediment (see scale in Fig 3). It is reasonable  
371 to expect some petrol Pb in the sediment as the  $^{210}\text{Pb}$  chronology indicates the top part  
372 of the sediment spanning through the 1990s and 2000s (Chen et al., 2016a), which  
373 represents an integration of historical freshwater environments in Singapore over the  
374 last 20 years. Case in point, the concentration of Pb in the surface sediments of  
375 MacRitchie falls in between the values for natural soils at the bottom of MacRitchie  
376 and those of the highest Pb from gas station soil (60, 2 and 95mg/Kg respectively)  
377 (Table 3).

378 The Pb isotopes in Singapore runoff show a moderate range, as  $^{206}\text{Pb}/^{207}\text{Pb}$  from 1.138  
379 to 1.169 and  $^{208}\text{Pb}/^{206}\text{Pb}$  from 2.096 to 2.125 (Table 2). The five samples almost form

380 a straight line on the triple isotope space ( $R^2=0.94$ , Fig 3). In contrast to the  
381 MacRitchie top sediment, most of the runoff sites have Pb isotopes overlapping with  
382 recent Singapore aerosols on the triple isotope space (Fig 3). Since industrial Pb is the  
383 main source in present day aerosols, the isotopic overlap between Pb in aerosol and  
384 runoff water indicates that the Pb in runoff water is also mainly from industrial  
385 activities. Comparing the current runoffs with the MacRitchie reservoir surface  
386 sediments, a transition of Pb sources from historically used leaded petrol to current  
387 industrial sources is observed.

388 Another feature in the runoff is that except for West Coast Park, the Pb isotope among  
389 sites are relatively homogenous, despite strong differences in land use (Table 2).  
390 Similar homogeneity was also found in Pb concentration in the road-deposited  
391 sediments in Singapore, as the Pb concentration in the sediments from industrial and  
392 residential sites were similar (Yuen et al., 2012). The homogeneity implies that the Pb  
393 among the sites comes from a similar source, which is likely to be aerosols. The  
394 concentrations of Pb we found in runoff waters were not homogeneous as the large  
395 range indicates (Table 3). This could be because of large concentrations in  
396 construction sites near Bukit Timah residential site, and accumulation of Pb and other  
397 metals in the Tuas industrial drainage canals sampled (Zn and Cd, not shown). These  
398 2 cases indicate that similarly industrial Pb is present in different concentrations at  
399 specific sites. To conclude from the isotopic homogeneity among sites and the  
400 isotopic agreement with aerosols, the Pb in Singapore runoff water is mainly from  
401 regional industrial sources through atmospheric deposition.

402 The water from West Coast Park (WCP) has the highest  $^{206}\text{Pb}/^{207}\text{Pb}$  (1.169) among  
403 the runoff sites (Table 2). On the triple isotope space, the WCP water deviates slightly  
404 from the aerosols towards natural Pb (Fig 3). The reason for higher  $^{206}\text{Pb}/^{207}\text{Pb}$  was

405 that the sample was taken in an estuary that constantly flushes with seawater. In fact,  
406 the Pb concentration measured there (20pmol/kg) was significantly lower than in the  
407 other sites, strengthening the hypothesis of seawater flushing. In contrast, the coastal  
408 waters taken at the nearby West Coast station show very high and variable  
409 concentrations (291 and 142pmol/kg for SW and NE monsoon) perhaps related to a  
410 marine gas station, heavy boat traffic, a mid-size shipyard and oil platform plants. The  
411 seawater in Singapore Straits has systematically higher  $^{206}\text{Pb}/^{207}\text{Pb}$  compared to runoff  
412 and will be discussed in the next section.

413

#### 414 Marine coastal environment

415 The seawater around Singapore has lead isotopes defined as  $^{206}\text{Pb}/^{207}\text{Pb}=1.180\pm 0.010$   
416 and  $^{208}\text{Pb}/^{206}\text{Pb}=2.091\pm 0.007$ , and the  $^{206}\text{Pb}/^{207}\text{Pb}$  in seawaters is higher than the  
417 runoff (Table 1). In triple isotope space, seawater falls between industrial Pb and  
418 natural Pb (Fig 3), implying that both industrial and natural Pb sources contribute to  
419 Singapore Straits seawater. Regardless of higher or lower concentrations, a linear  
420 mixing trend is found for all data points. The contribution of natural Pb to Singapore  
421 Straits water ranges from ~20% to ~70% (see the scale in Figure 3).

422 Although we found seasonal differences in  $^{206}\text{Pb}/^{207}\text{Pb}$  for our aerosol samples (Fig 2),  
423 no clear trend was found for the coastal seawater samples (Fig 4; Supplementary  
424 Table 3). Over a two-year sampling period (2011-2013) (Table 2; Chen et al., 2016c),  
425 the average  $^{206}\text{Pb}/^{207}\text{Pb}$  was almost identical in the NE ( $1.179\pm 0.011$ ) and the SW  
426 ( $1.180\pm 0.010$ ) monsoons, implying a lack of seasonality in seawater Pb. However,  
427 Chen et al. (2016c) have previously proposed an isotope exchange mechanism that  
428 could be affecting the results we see here. In brief, crustal particulates with natural Pb  
429 isotopic composition are delivered to Singapore waters by rivers in this region, and

430 the Pb on crustal particulates exchanges with the Pb in seawater and alters the  
431 seawater Pb isotopes towards natural values. The isotope exchange seems to operate  
432 in a much shorter timescale than the residence time of Pb in the Singapore Straits,  
433 therefore maintaining the Pb isotope in Singapore Straits' water (Chen et al., 2016c).  
434 The proposed isotope exchange mechanism is also supported by the high  $^{206}\text{Pb}/^{207}\text{Pb}$   
435 observed in Johor River mouth (Supplementary Table 3), which should have the  
436 highest concentration of crustal particulates. While we cannot at this point draw any  
437 solid conclusions regarding Pb sources Singapore's coastal seawater, our results  
438 suggest more local mechanisms driving Pb isotopes in coastal waters – be it through  
439 isotope exchange, or the mixing of multiple Pb sources.

440

441 Geographically, stations in the Johor Straits (Kranji, Seletar, Sembawang, Punggol)  
442 show slightly lower  $^{206}\text{Pb}/^{207}\text{Pb}$  than those from the Singapore Straits in both seasons  
443 (Fig 4; Supplementary Table 3), indicating more industrial Pb contribution to the  
444 northern coastal water. The greater contribution of industrial Pb in the North might  
445 not be caused by more industrial activities as the main industrial area in Singapore is  
446 located on the southwest side of Singapore near Tuas, which shows  $^{206}\text{Pb}/^{207}\text{Pb}$   
447 towards natural sources (Supplementary Table 3). Instead, the likely reason for the  
448 lower  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios is that less flushing takes place in the North due to the  
449 causeway, a dam in the middle of the Johor Straits which interrupts water transport  
450 from West to East (see Fig 1). As the water in the North is relatively stagnant, the  
451 atmospherically deposited industrial Pb could not be flushed away easily, resulting in  
452 an apparent greater contribution of industrial Pb compared to the South. Higher Pb  
453 concentration in the surface sediments in the Johor Straits, particularly close to the  
454 causeway also supports limited flushing (Yap et al., 2010). We found higher

455 concentrations in the coastal waters in the Johor Straits in comparison with those in  
456 the Singapore Straits (except West Coast Park and Tuas North sites, both located near  
457 sites of industrial activity), further supporting this hypothesis. The averages for Johor  
458 Straits and Singapore are 164 vs 80pmol/kg for the SW monsoon, and 94 vs  
459 98pmol/kg for the NE monsoon respectively, suggesting an accentuated effect of  
460 limited flushing in the SW monsoon season.

461

## 462 CONCLUSION

463 We provide an updated view of sources and variability of Pb in Singapore through  
464 exploring the Pb isotopes and concentrations in various environments, including  
465 aerosols, incineration ashes, reservoir sediments, gas station soil deposits, runoff  
466 water and coastal seawater. Among these sites, the end-members have been identified  
467 as leaded petrol, industrial Pb and natural Pb. The three end-members contribute in  
468 various proportions of Pb in Singapore's ambient environment. In the atmospheric  
469 environment, the Pb in Singapore aerosols is now mainly from regional industrial  
470 sources with some transboundary Pb influence indicated by the seasonal variability. In  
471 the freshwater environments, we observe a transition of Pb sources from historically  
472 leaded petrol in the 1990s to regional industrial sources in the present day. The Pb in  
473 Singapore's freshwater environments is likely brought through atmospheric  
474 deposition. As such, in a post-leaded petrol Singapore, the concentrations in reservoirs  
475 has shown to be below WHO drinking water standard (Chen et al., 2016a). In the  
476 coastal environments, we observe significant contributions of Pb from both natural  
477 and industrial sources that could be linked to the different water flushing intensity in  
478 the Johor and the Singapore Straits. Natural sources contribute from 20%-70% of Pb

479 in Singapore coastal water. Isotope exchange could potentially be the mechanism for

480 the large contribution of natural Pb to the coastal water.

481

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493 Utilities Board granting access to the drainage channels on sampling. The Pb and Pb  
494 isotopes data in this study included in the tables and any additional data associated  
495 with this study may be obtained from Dr. Mengli Chen (email: [mlchen@ntu.edu.sg](mailto:mlchen@ntu.edu.sg)).

496

497 Contribution

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

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

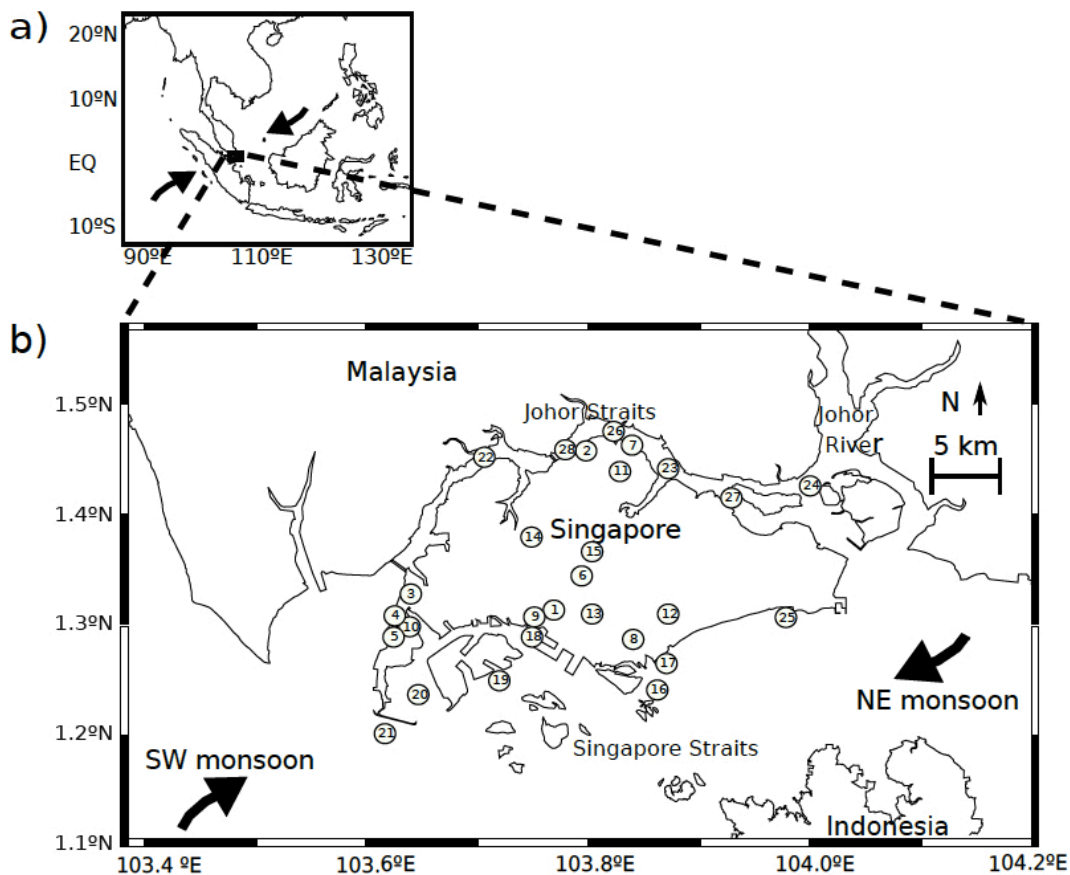
501 Edward A. Boyle analysed some samples, provided resources and supervision on the  
502 project.

503 Jani Tanzil took some samples and performed the statistical analyses.

504 Kuanbo Zhou took some samples, edited the manuscript

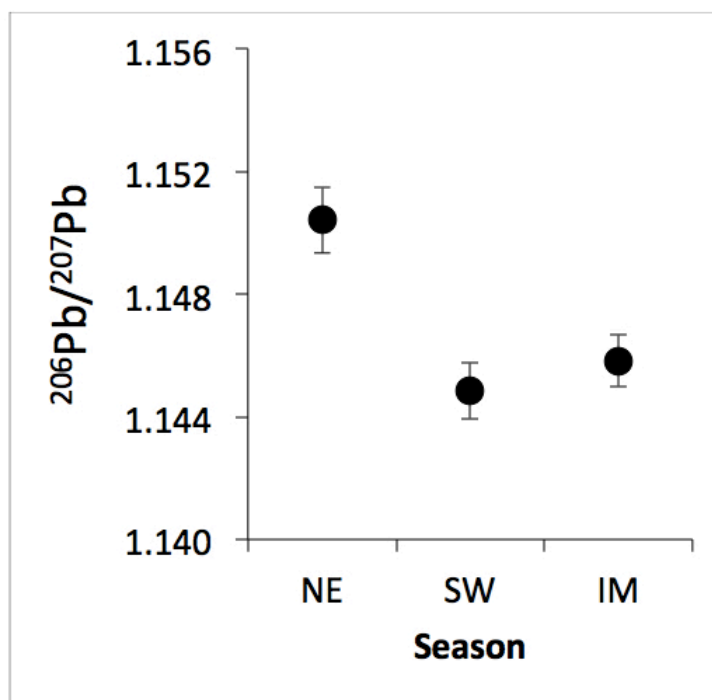
505 Nathalie F. Goodkin provided resources and supervision on the seawater sampling  
506 cruises.

507



509

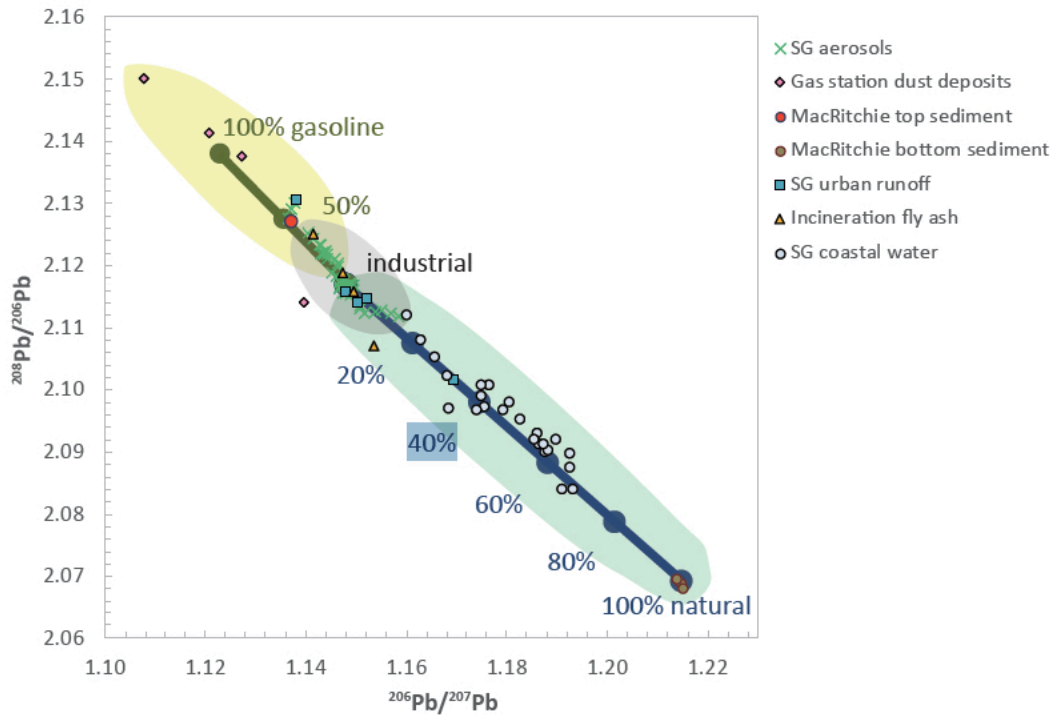
510 Figure 1: Map of the sampling sites. (a) Singapore's relative location within Southeast  
 511 Asia. Arrows denote monsoonal wind directions. (b) Sampling sites within and  
 512 around Singapore. Aerosols from sampler at National University of Singapore (1); ash  
 513 samples from incinerator plants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



522

523 Figure 2:  $^{206}\text{Pb}/^{207}\text{Pb}$  in aerosol samples collected during the northeast monsoon (NE;  
524 December–March), southwest monsoon (SW; June–September) and inter-monsoon  
525 (IM; April–May and October–November) periods. Error bars denote  $\pm 1\text{SE}$ . ANOVA  
526 and Tukey's post-hoc show NE monsoon  $^{206}\text{Pb}/^{207}\text{Pb}$  to be significantly higher than  
527 that found for SW monsoon and IM periods.

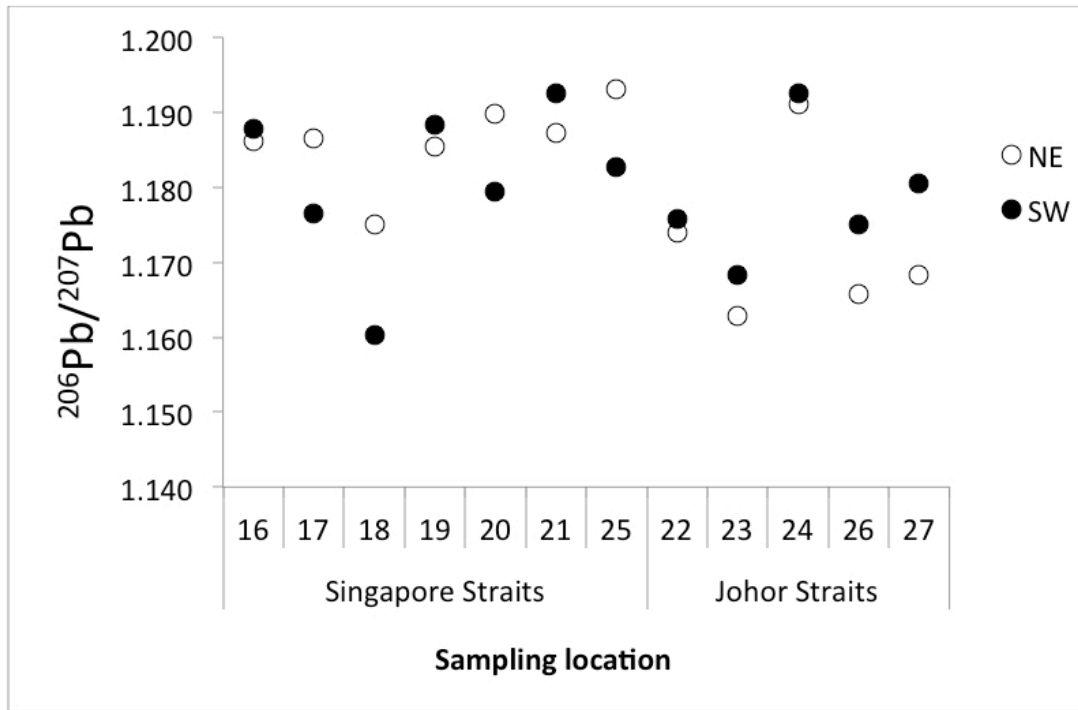
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529

530 Figure 3: Triple isotope plot for the Pb in Singapore environments, including aerosols  
 531 (green crosses), gas station dust deposits (pink diamonds), MacRitchie top and bottom  
 532 sediments (red and green circles), runoff water (blue squares), incineration fly ash  
 533 (yellow triangles) and coastal water (open circles). The three identified end-members  
 534 are illustrated as gasoline, industrial and natural. The olive-coloured scale bar display  
 535 the percentage contribution of gasoline if taking the identified 'gasoline' and  
 536 'industrial Pb' as end-members, the blue-coloured scale bar display the percentage  
 537 contribution of natural Pb if taking the identified 'natural Pb' and 'industrial Pb' as  
 538 end-members. Shaded areas differentiate the contribution from the three identified  
 539 end-members and are for illustration only.

540



541  
 542 Figure 4:  $^{206}\text{Pb}/^{207}\text{Pb}$  in coastal seawater samples collected during the northeast  
 543 monsoon (NE; December–March) and southwest monsoon (SW; June–September)  
 544 from sampling locations around Singapore (along the Johor and Singapore Straits).  
 545 Kusu island (16), central business district (17), West Coast (18), Jurong island (19),  
 546 Tuas North (20), Tuas South (21), Kranji (22), Seletar (23), Johor River mouth (24),  
 547 Changi (25), Sembawang (26), Punggol (27). See Figure 1 for map of sampling  
 548 locations.  
 549  
 550

551 Table 1: An overview  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio among the sampled environments. End-

552 members are identified.

553

<u>Name</u>	<u>Year samples represent</u>	<u>206/207 range</u>	<u>206/207 average</u>	<u>Representing End-member</u>	<u>Source</u>
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

554

555

556 Table 2: Pb isotope in Singapore runoff water.

*Runoff*

<i>Name</i>	<i>206/207</i>	<i>2SE</i>	<i>208/207</i>	<i>2SE</i>	<i>208/206</i>	<i>2SE</i>	<i>Land use</i>
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

557

558

559 Table 3: Pb concentrations in Singapore gas station soils (mg/Kg), runoff water  
 560 (pmol/kg) and coastal water (pmol/kg).

561

Gas station soil deposits

<u>Name</u>	<u>Pb (mg/Kg)</u>
Shell Havelock	95.1
Shell Geylang	9.9
ESSO Bukit Batok	23.6
ESSO Yishun	35.9
Mean	41.1

562

Runoff

<u>Name</u>	<u>Pb (pmol/kg)</u>
Bukit Timah Rd	293
Sembawang Park	37
Raffles place	160
West Coast Park	20
Tuas	1047
Mean	311

563

564 Coastal seawater

<u>Name</u>	<u>SW monsoon (July 2015) Pb (pmol/kg)</u>	<u>NE monsoon (Dec 2015) Pb (pmol/kg)</u>
Kusu	108	108

CBD	82	146
West Coast	291	142
Jurong island	45	90
Tuas North	175	181
Tuas South	110	101
Kranji	56	44
Seletar	216	47
Johor River mouth	266	137
Changi	115	65
Sembawang	77	65
Punggol	143	73
Woodlands	-	174
Mean	141	106

565

566

567 Supplementary Table 1: Temporal variability of Pb isotope in Singapore aerosols.

568 Data from Chen et al. (2016)a.

569

<i>Sampling period</i>	<i>206/207</i>	<i>6/7 2SE</i>	<i>208/206</i>	<i>8/6 2SE</i>
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

570

571

572 Supplementary Table 2: Pb isotope in incineration ash from incinerators (from Chen  
 573 et al., 2015) and gas stations soil deposits (this study) around Singapore.

574

*Incineration ash*

<i>Incinerator</i>	<i><u>206/207</u></i>	<i><u>2SE</u></i>	<i><u>208/207</u></i>	<i><u>2SE</u></i>	<i><u>208/206</u></i>	<i><u>2SE</u></i>
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*

<i>Name</i>	<i><u>206/207</u></i>	<i><u>2SE</u></i>	<i><u>208/207</u></i>	<i><u>2SE</u></i>	<i><u>208/206</u></i>	<i><u>2SE</u></i>
Shell Havelock	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 Bukit Batok	1.1209	0.0001	2.3944	0.0004	2.1362	0.0002
ESSO Yishun	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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581 Supplementary Table 3: Pb isotope in Singapore coastal water as shown in Fig 4.

582

*SW monsoon coastal water*

*(July 20-22, 2015)*

<i>Name</i>	<i>206/207</i>	<i>2SE</i>	<i>208/207</i>	<i>2SE</i>	<i>208/206</i>	<i>2SE</i>
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*

*(December 17-18, 2015)*

<i>Name</i>	<i>206/207</i>	<i>2SE</i>	<i>208/207</i>	<i>2SE</i>	<i>208/206</i>	<i>2SE</i>
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

583

584 • excluding Woodlands for the average as it was sampled on one season only

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586

587 6. References

588

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